THE DEVELOPMENT AND INVESTIGATION OF NEW CHIRAL GOLD(I) CATALYSTS

A Thesis Submitted for the Degree of
Doctor of Philosophy

By

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Abstract

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Metal-catalysed reactions are highly attractive processes due to their atom economy and open opportunities in the development of new transformations.

In the introduction, the theoretical aspects of gold(I) catalysis with examples of gold(I) complexes and their transformations are described with emphasis on enantioselective synthesis.

The results and discussion chapter begins with the investigations of a chirally active counterion moiety. The triflic amide moiety was found to be an efficient new counterion and provide opportunity to introduce chiral bidentate ligand on gold(I) complexes.

In conclusion, a series of chiral bidentate gold(I) catalysts were synthesised and their catalytic activity demonstrated on model transformations. A number of strategies improve a bidentate ligand for gold(I) catalysts.

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Abbreviations

Techniques

DFT	Density Functional Theory
DOSY	Diffusion-Ordered Spectroscopy
EI	Electron Impact
FAB	Fast Atom Bombardment
HPLC	High-Performance Liquid Chromatography
MS	Mass Spectroscopy
NMR	Nuclear Magnetic Resonance
TLC	Thin Layer Chromatography

Reagents and solvents

4-DMAP	4-dimethylaminopyridine
Ac	acetyl
Ad	adamantyl
Alloc	allyloxycarbonyl
Bn	benzyl
Boc	*tert*-butyl carbamate
Bpoc	2-(4-biphenyl)isopropoxycarbony
Bsmoc	(1,1-dioxobenzo[b]thiophene-2-yl)methyloxycarbonyl
Bts	benzothiazole-2-sulfonyl
Bz	benzoyl
Cbz	carboxybenzyl
CCD	dicyclohexylcarbodiimide
CDI	1,1'-carbonyldiimidazole
Cy	cyclohexane
DABCO	1,4-diazabicyklo[2.2.2]octane
DCE	1,2-dichloroethane
DCM	dichloromethane

Ddz	**α**,**α**-dimethyl-3,5-dimethoxy- benzyloxycarbonyl
DMF	dimethylfomamide
DMSO	dimethyl sulfoxide
E	electrophile
EDC	1-ethyl-3-(3-dimethylaminopropyl) carbodiimide)
Esc	ethanesulfonylethoxycarbonyl
Et	ethyl
Et_2O	diethyl ether
EtOH	ethanol
EWG	electron withdrawing group
Fmoc	9-fluorenylmethoxycarbonyl
h	hour(s)
HOBt	hydroxybenzotriazole
HOMO	highest occupied molecular orbital
i-Bu	isobutyl
IMes	1,3-bis(2,4,6-trimethyphenyl)imidazole-2-ylidene
i-Pr	isopropyl
LG	leaving group
LUMO	lowest unoccupied molecular orbital
MCPBA	*meta*-chloroperoxybenzoic acid
Me	methyl
MeOH	methanol
Mes	mesityl
n-Bu	*n*-butyl
Nps	2-nitrophenylsulfenyl
Nsc	2-(4-nitrophenylsulfonyl)ethoxycarbonyl
Nu	nucleophile
*o*NBS	*ortho*-nitrobenzenesulfonyl
OPNB	*para*-nitrobenzoate
PET	‘petroleum ether’- very volatile, narrow alkene hydrocarbon distillate
Ph	phenyl

Piv	pivaloyl
RT	room temperature
TBAF	tetra-*N*-butylammonium fluoride
TBDPS	*tert*-butyldiphenylsilyl
TCP	tetrachlorophthaloyl
TDA-1	tris(2-(2-methoxyethoxy)ethyl)amine
tert-Bu	*tert*-butyl
Tf	triflyl
THF	tetrahydrofuran
TMS	trimethylsilyl
Tol	*para*-tolyl
Trt	triphenylmethyl
Ts	*para*-toluenosulfonyl

1. Introduction

In 1836, Swedish chemist Jöns Jacob Berzelius introduced the term 'catalysis'.[1] The word is taken from Greek *katalusis* meaning: *dissolution.*

A catalyst is a compound, which promotes a chemical process through the reduction of the activation energy thus increasing the speed of the reaction. It does not however change the thermodynamics of the reaction. During the reaction, the catalyst is not consumed and it does not undergo permanent chemical transformation.[2]

The three main types of the catalysis are recognized:

- Heterogeneous – the catalyst is in a different phase and the reaction occurs at the surface of the catalyst (transition metal) where molecules are adsorbed.
- Enzymatic – the catalyst is enzyme based.
- Homogeneous – the catalyst and substrate are in the same phase where intermediate species are formed where the oxidation state of transition metal changes.

1.1 Theoretical Aspects of Gold Homogeneous Catalysis

For many years chemists considered gold as a transition metal with low catalytic activity. This misconception resulted that for almost 70 years gold had lived in the shadow of other metals.[2]

In organic chemistry, gold is not used in its elementary state, but as a complex. The main oxidation states in gold chemistry are Au(I) and Au(III) with the electronic configuration $[Xe]5d^{10}6s^{0}6p^{0}$ and $[Xe]5d^{8}6s^{0}6p^{0}$ respectively, however the oxidation states of gold can vary from (-I) to (V). The relativistic theory has helped to rationalise some of the properties of gold.[3] The theoretical work of Schrödinger and Dirac gave underpinning for relativistic effects theory. A post-lanthanide atomic nucleus contains large number of protons, which means that electrons move in a field of very high nuclear charge. The consequence of this is that the velocity of electrons approach the speed of light and consequently, they have to be treated according to Einstein's theory. This is particularly true for electrons in the *s* and *p* orbitals due to the fact they are closer to the nucleus and have greater ionization energies, but less important for electrons in *d* and *f* orbitals, which

are shielded by electrons in *s* and *p*. This effect weakens nuclear attraction and as a consequence the expansion of the 5*d* and 4*f*.[3] The effect on the 6*s* and 6*p* orbitals, in the post-lanthanide elements, is that the orbital radius is contracted and the distance of the electron from the nucleus is reduced. The consequence of this is the unique colour of gold. The excitation from the 5*d* filled band to 6*s* band (bandgap 2.38 eV) corresponding to the absorption of blue visible light and reflects red and yellow. Another consequence is the *aurophilicity*.[4] The closed shell $5d^{10}$ in gold(I) is no longer chemically inert and can interact with other elements (such as other gold atoms). The two gold(I) centres with equal charge can form $5d^{10}$ - $5d^{10}$ interactions with an equilibrium distance of 3.003 Å average. The formation of oxidation state III can be explained by the destabilisation of the 5*d* orbitals while the formation of gold(-I) can be a consequence of the stabilization of 6*s* orbital.

Another even more important consequence is that gold complexes are excellent Lewis acids. The strong Lewis acidity correlates with electronegativity and in the case of gold (2.54 referred to the Pauling scale) is a result of relativistic contraction of the 6*s* and 6*p* orbitals (which correspond to the lowest unoccupied molecular orbital – LUMO). Additionally, the large cation of Au(I) can be considered to be "soft" Lewis acid, reacting preferentially with "soft" species (such as π- systems) and being less oxophilic. The study of Au(I) complexation showed greater stabilisation for the ethylene complex then ethyne complex over 10 kcal mol^{-1}.[5] The complexation of the alkynes of Au(I) is apparently not selective over other alkenes. This observation can be rationalised by discrimination of approaching nucleophile between Au(I)-activated electrophiles.[3] The selectivity can be explained by energy level of LUMO in ethyne and ethylene. Alkynes have lower HOMO and LUMO than alkenes, and it is assumed than an alkyne-Au complex has a lower LUMO energy than an alkene-Au complex, making it more reactive towards nucleophilic attacks.[6]

Gold(I) has a $5d^{10}$ outer shell electron configuration complexes with a linear, two-coordinated geometry with neutral, positively- or negatively-charge, depending on the ligands (thiolates, thioethers, phosphines, cyanide, alkyl groups and nitrogen donor ligands such as amines and heterocycles). The most common form of gold(I) however is

three-coordinated (normally containing at least one neutral ligand and have trigonal planar geometry), four coordinated (tetrahedral coordination) are also known.[7]

The monodantate ligand exchange bound to gold(I) occurs generally rapidly *via* an associative mechanism through a three-coordinate transition state.[8]

The gold(III) are a $5d^8$ outer shell electron configuration complexes and forms four-coordinate, square-planar complexes. The bond lengths between gold(III) and ligands are generally shorter in comparison with gold(I). The overall charge of gold(III) complexes depends on the type of ligand (with four neutral ligand the resulting complex has +3, while with four negative ligands the charge is -1.[7]

1.2 Dewar-Chatt-Duncanson Model - Π- Complexation

In the 1950s M. J. S. Dewar and J. Chatt proposed donor-acceptor theory which explained the bonding between a Pt centre to the ethylene molecule in Zeise's salt (Figure 1), nowadays known as the Dewar-Chatt-Duncanson model.[9,10]

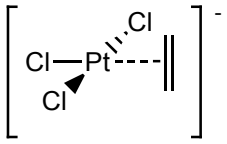


Figure 1

The theory assumes that the π-type bond of the alkene donates electron density from the bonding orbital between the carbon atoms into d-orbital of the metal atom and the metal atom donates electrons back into the empty π∗ antibonding orbital from the filled d-orbital.[10] These two interactions give rise to elongated C-C bond and a lowering of the vibration frequency. This leads to the activation of C-C multiple bond – the basis of metal catalysis.

The studies on π-complexation showed that mercury compounds catalyse the addition reactions of alkenes and alkynes (the activation for nucleophilic attack).[11,12] The activity of mercury and platinum led scientists to the conclusion that the gold could have catalytic activity.

1.2.1 Gold(I) Complex with Alkyne

In the literature, two types of gold(I) complexes with an alkyne were found: neutral gold(I)/alkyne complex and cationic gold(I)/alkyne with and without co-ligands.

In the 1970's, Hüttel reported the first neutral gold(I) complex with alkynes containing the general formula $(yne)_nAuX$ where X represents the alkyne or an anionic ligand.[13] Generally, these type of compounds appear to be very unstable above 0 °C and only few were characterised well. The strained cyclic compounds showed higher stability and were reported by Wittig, Fisher[14] and Fürstner.[15] In 2009 Kroll and colleagues described a new type of neutral gold(I) complex (Figure 2).[16] The gold atom is coordinated with two nitrogen atoms to create bidentate X-L ligand type.

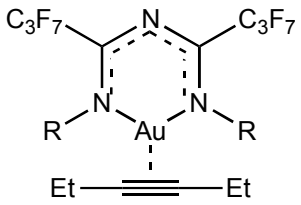


Figure 2

The cationic gold(I) with the alkyne and without ligand L, has only been observed in gas phase by Echevarren.[17] In 1998, Teles proposed cationic gold type $[(R_3P)Au(alkyne)]^+$ as an intermediate in catalytic addition of alcohols to the alkynes.[18] The complex was not isolated, however further investigation of a tertiary phosphine, prepared by Shapiro and Toste,[19] gave the first stable dimer complex of the gold(I) (Figure 3) complexed, head-to-tail through a flexible chain containing a triple bond attached to one of the phenyl group. The di-nuclear di-cation was successfully crystallised and its structure proved via X-ray crystallography. [19]

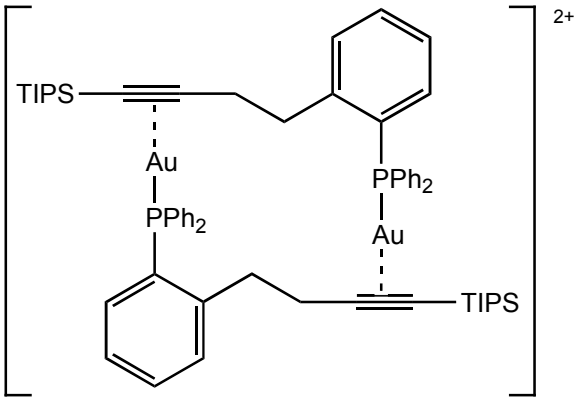


Figure 3

The most remarkable (yne)Au(I)XL type of compound was observed by Schulte and Behrens (Figure 4).[20] The complex appeared to be air-stable only for short time but in solution decomposition occurred slowly even compound was exposed on the air or light. The solubility in tetrahydrofuran or dichloromethane was poor due to the polymeric character of the compound. Only strongly coordinating solvents such as dimethyl sulfide/dichloromethane solution dissolved the compound.

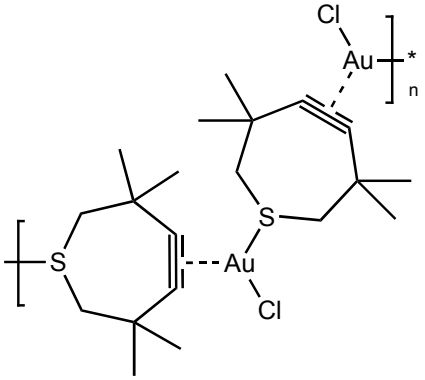
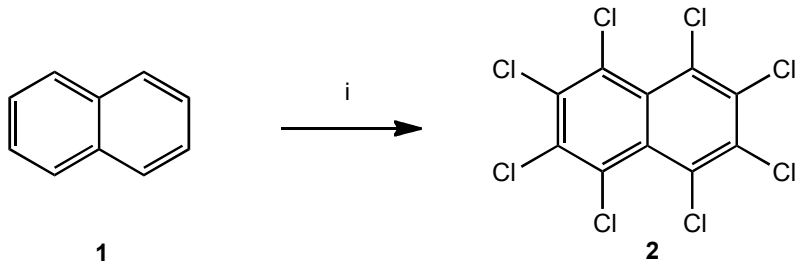


Figure 4

1.3 Racemic Reaction Catalysed by Gold

One of the earliest reports of a gold compound being used as a catalyst, was submitted by Schweberger and Gordon in 1935.[21] They used Au(I) and Au(III) in the polychlorination of naphthalene (**1**) occurred on all hydrogen atoms of naphthalene and octachloronaphtalene (**2**) was obtained as a product (Scheme 1).



1 **2**

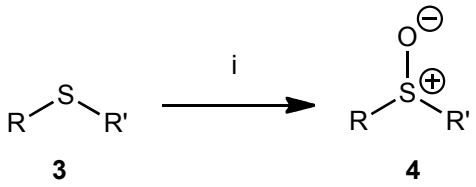
Reagents: i) AuCl or $AuCl_3$, Cl_2.

Scheme 1

Today, this reaction can be performed in the presence of cheaper Lewis-acid catalysts.[22]

1.3.1 Oxidation Reaction

In 1983 Natali described the first catalytic oxidation of a sulfide (**3**) to a sulfoxide (**4**) (Scheme 2) using a gold(III) chloride complex with a tetrabutylammonium cation as a catalyst (0.02 – 0.05 mol%).[23]



3 **4**

Reagents: i) $Bu_4N(AuCl_4)$, H_3CNO_2/HNO_3.

Scheme 2

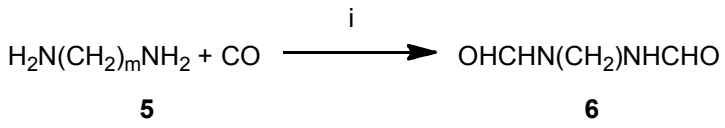
Phase-transfer conditions were used to achieve the desired transformation. Nitromethane, the only suitable organic solvent gave a relatively fast reaction rate at ambient temperature. The redox process in the organic phase is shown in Scheme 2. In the aqueous phase, the colourless Au(I) is reoxidised to the yellow Au(III) species (Scheme 3).

$$2NO_3^- + 3AuCl_2^- + 6Cl^- + 8H_3O^+ \longrightarrow 2NO + 3AuCl_4^- + 12H_2O$$

Scheme 3

Generally the reaction of aryl and alkyl sulfides proceeded in high yield, from 82 to 97%.[23,24]

Further examples of gold-based catalysts are Ph_3PAuCl, $(Ph_3P)_2AuCl$, Ph_3PAuNO_3 and $(Ph_3PAu)_2S$ all of which have been used by Deng.[25] The carbonylation of aliphatic diamine (**5**) in the presence of oxygen and carbon monoxide gave appropriate diformamide (**6**) (Scheme 4). The amount of catalyst used was between 0.75-1.6 mol%. The authors discovered that oxygen had a significant impact on the selectivity of the reaction and maintained the gold catalyst in the appropriate state. The temperature of the process was between 150-200 °C. The reaction achieved yield up to 99% using appropriate condition involving ratio between oxygen : carbon monoxide, solvent and temperature.



Reagents: i) $[Au(Ph_3P)_a]_bX$, O_2.
m = 6 or 8; a = 1 or 2; b = 1 or 2; X = Cl, NO_3 or S

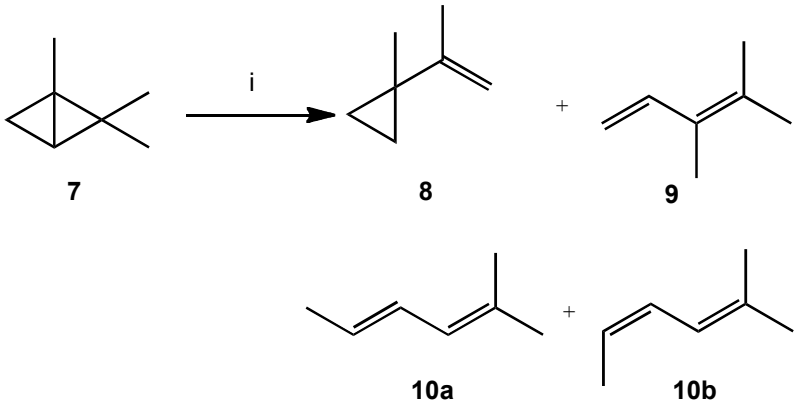
Scheme 4

In 2001 Shul'pin reported the efficient oxidation of alkanes using hydrogen peroxide in the presence of $NaAuCl_4$ (III) and Ph_3PAuCl (I) as a catalyst. The reactions were conducted in an acetonitrile solution at 75 °C with the main product being an alkyl hydroperoxide. However, small concentrations of the related ketones (aldehydes) and alcohols were obtained.[26] Further investigation showed that the presence of $AgClO_4$ in the oxidation caused it to proceed more rapidly. This implied that Au(I) was an active species after elimination of one or more anions, accelerated by the silver derivative. The authors suggested that the oxidation began from the alkane hydrogen atom abstraction by the gold oxo-complex Au(III)=O.

1.3.2 C-C Bond Formation

1.3.2.1 Strained Compounds

During the investigation of the transition metal complex promoted rearrangement of methyl-substituted bicyclo[1.1.0]butanes (**7**) (Scheme 5), Gassman (1972) found that the product obtained depended on the transition metal, the oxidation state and ligands attached to the metal.[27] A similar ratio of products (**8-10**) was obtained with AuI_3 as $PdCl_2$ (d^8-system like Au(III) - d orbital with 8 electrons). Author suggested that transition metal complex behaves as a specific Lewis acid producing the most stable cyclopropylcarbinyl cation.



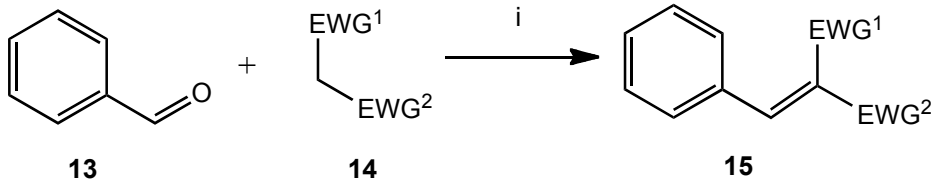
Reagents: i) AuI_3 (3.7 mol%), $CHCl_3$.

Scheme 5

1.3.2.2 Knoevenagel condensation

In 1996, Komiya described Au(I)- and Au(III)-alkoxides that could be used to catalyse a Knoevenagel condensation.[28] The reaction used Au(OR)(L) (**11**) or $Au(OR)(Me)_2)(L)$ (**12**) as the catalysts where R = CH_2CF_3, $CH(CF_3)_2$ and L = PPh_3, PCy_3 respectively. The substituents L had a little influence on the activity of the catalysts however, more electron-withdrawing counterion hexafluoroisopropoxide increased the activity of the catalysts. These compounds both appeared basic, nucleophilic and capable of removing a proton from various organic compounds such as alkylcyanoesters which transfer to very stable α-carbonyl organogolds: intermediates in catalytic Knovevenagel condensation. These organogold compounds react with benzaldehyde to produce

stoichiometric selective carbon-carbon bond. The author also used alkyl cyanoacetates (**14**) and benzaldehyde (**13**) in the investigation (Scheme 6). The yield of **15** was very good, between 81-93%.

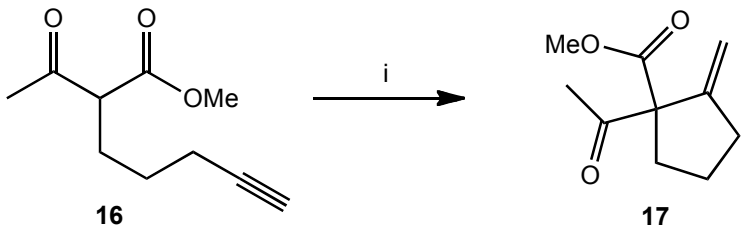


Reagents: i) **11** or **12** (10 mol%), DMSO.
EWG^1, EWG^2 = CO_2R, CN

Scheme 6

1.3.2.3 Conia-ene reaction

The one of the most powerful methods for forming C-C bonds is the alkylation of an enolate. The Conia-ene reaction provides access directly to α-functionalise ketones, however it does require high temperatures.[29] Transition metal catalysts[30] such as Pd,[31] Mo [32] or Cu [33] have been used to catalyse this reaction at lower temperatures, but generation of an enolate is required. In 2004, Toste presented a catalytic version of Conia-ene reaction using phosphine gold(I) complexes (PPh_3AuCl, $(CyNC)_2AuPF_6$, $[(PPh_3Au)_3O]BF_4$ – without success and $[(PPh_3Au)_3O]BF_4$ with 5% HOTf and PPh_3AuOTf with very good yield) under neutral condition (at ambient temperatures).[34,35] The ketoester **16** was used as the starting material (Scheme 7).[35]



Reagents : i) catalyst, DCE.

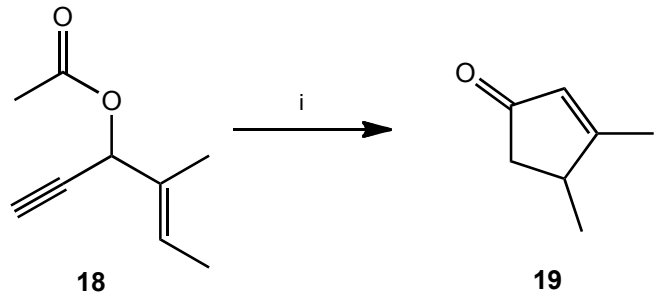
Scheme 7

Optimisation of reaction with $(Ph_3P)AuOTf$ in DCM showed that 1 mol % of gold(I) catalyst rapidly converted ketoester **16** into cyclopentene **17** in 94% and the

catalyst can be used in "open-flask" conditions. Wide ranges of ketoester substrates were converted under these conditions. Longer reaction times were required when the substituents on the ketone were increased in size, although altering the ester group from methyl to *tert*-butyl had minimal impact.

1.3.2.4 Rautenstrauch rearrangement

In 2005 Toste reported the formation of cyclopentenones using gold(I) complex[36] via Rautenstrauch rearrangement.[37] Treatment of compound **18** with 5 mol% of $Ph_3PAuOTf$ in DCM afforded cyclopentenone **19** (Scheme 8) in only 30 % yield. The investigation of the solvent effect showed that by using CH_3CN the yield of **19** could be improved (Table 1).



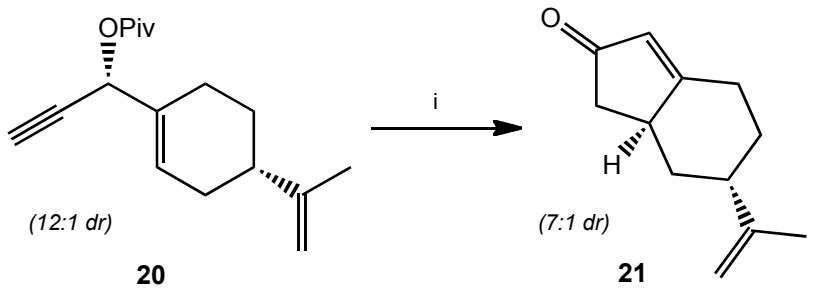
Reagents : i) 5 mol% $Ph_3PAuOTf$, solvent (Table 1), R.T.

Scheme 8

Table 1

Entry	R	Solvent	Time	Yield [%]
1	Me	CH_2Cl_2	0.5h	30
2	Me	CH_3CN	6h	77
3	Ph	CH_3CN	6h	76
4	*t*-Bu	CH_3CN	6h	100

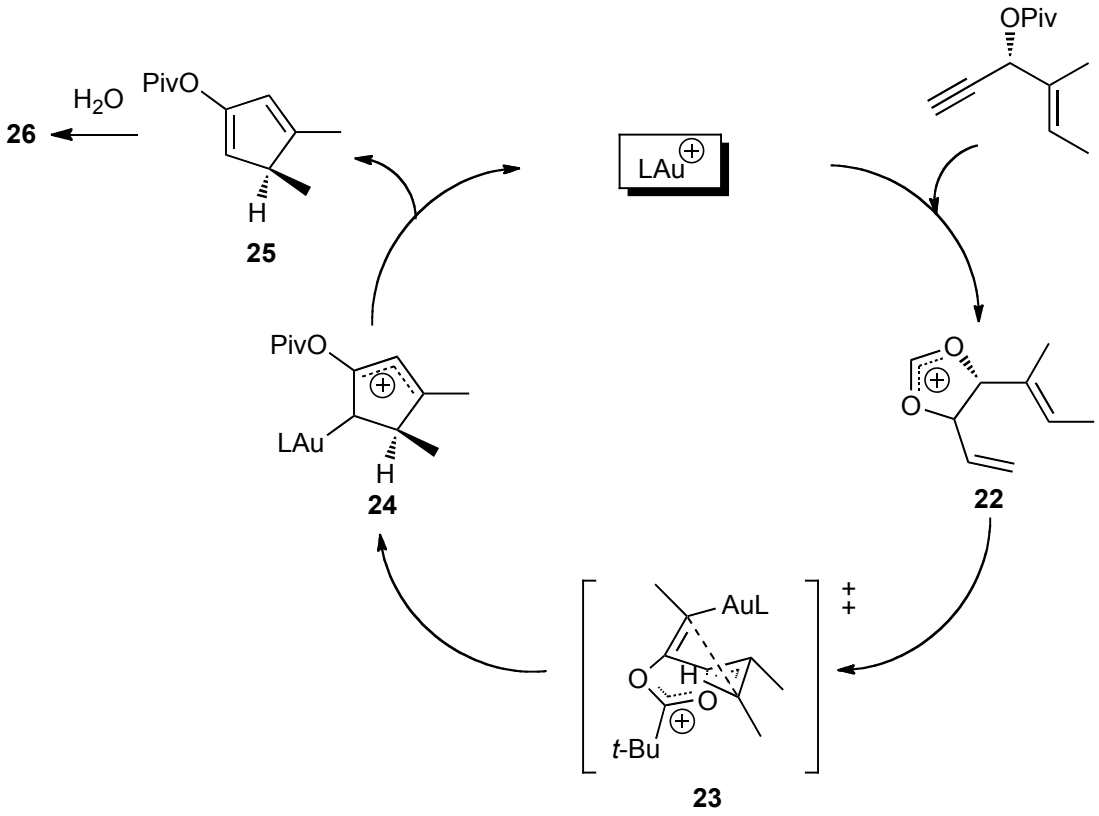
The change of the ester from an acetate to a pivaloate also showed an improved yield. The attempt with chiral compound **20** suggested that stereochemistry of the starting ester was transferred into the product **21** (Scheme 9).



Reagents : i) 2 mol% $Ph_3PAuOTf$, CH_3CN, R.T.

Scheme 9

The ranges of chiral propargyl pivaloates were prepared and examined. The enantiomeric excess was clearly improved through the switching the counter ion, from OTf to SbF_6 and lowering of the temperature to -20 °C. The authors proposed a mechanism of the Au(I)-catalysed cyclopentenone synthesis via vinyl gold species **22** followed by stereoselective intramolecular cyclisation (**23**). The cyclisation produced a cationic intermediate **24** by losing cationic gold(I), which afforded diene **25**. The final compound **26** is then obtained by hydrolysis (Scheme 10).



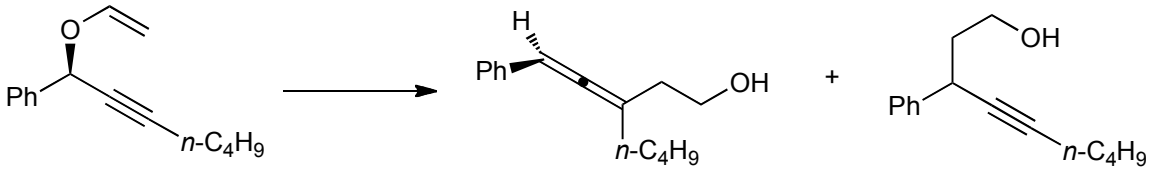
Scheme 10

1.3.2.5 Acetylenic Claisen Rearrangement

Claisen rearrangement can be catalysed by Lewis acids, which can be divided into two classes:

1. Hard Lewis acids, catalysed rearrangement by coordination to vinyl ether oxygen.[38-40]
2. Soft Lewis acids, catalysed rearrangement by coordination to the π-bonds.[41,42]

The second class is often limited by preventing the activation of allylic olefin caused by strong bonding of the electrophilic metal to nucleophilic vinyl ether. In 2004 Toste proved that the problem does not occur when Au(I) complex is used as a catalyst in an acetylenic Claisen rearrangement.[43] The propargyl vinyl ether **27** as the starting material and three catalysts based on triphenylphospin gold cation with different counterions were examined (Scheme 11).



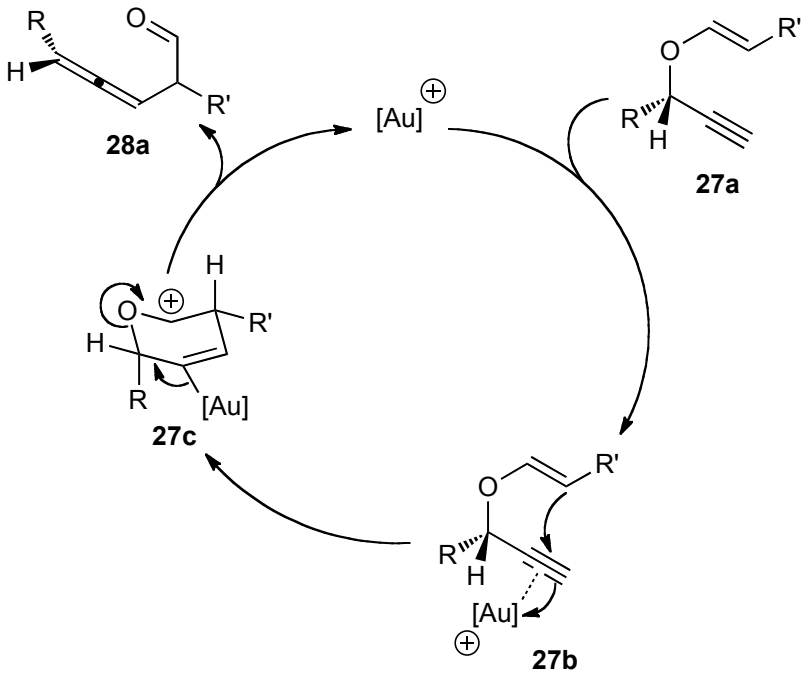
27 **28** **29**

cat. = $Ph_3PAuOTf$	1.7 (44%, 82% *ee*)	1.0
Ph_3PAuBF_4	> 20 (85%, 4% *ee*)	1.0
$[(Ph_3PAu)_3O]BF_4$	> 20 (91%, 90% *ee*)	1.0

Reagents: i) 1% cat., CH_2Cl_2, 10 min., R.T.; ii) $NaBH_4$, MeOH, R.T.

Scheme 11

The Claisen and [1,3] rearrangement products (**28** and **29**) were obtained with different ratios. Surprisingly, the chirality from the starting material was transferred to the Claisen rearrangement product. The gold-oxo complex $[(Ph_3PAu)_3O]BF_4$ (inactive in the Conia-ene reaction described in Chapter 1.3.2.3, p. 16) appeared to be the most efficient with nearly complete chirality transfer. The range of substrates containing electron rich and electron efficient aryl group and alkyl group at the propargyl position were examined and afforded good to excellent yield.

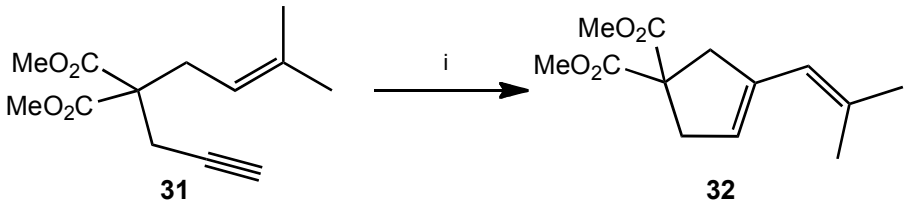


Scheme 12

The proposed mechanism (Scheme 12) started with a 6-*endo*-dig addition of the enol ether **27a** onto the gold(I)-alkyne complex **27b** affording formation of intermediate **27c**. The Grob-type fragmentation of **27c** leads to the *β*-allenic aldehyde **28a** and recovered the gold catalyst.

1.3.2.6 Cycloisomerisation of Enyne

In 2005, Gagosz reported a new phosphine gold(I) complex with bis(trifluoromethanesulfonyl)imidate as a coordinating counterion.[44] The new compound appeared as an equivalent of the old systems of the phosphine gold(I) chloride complex and silver salt as a co-catalyst which give limitations (as it is very hygroscopic). The bis(trifluoromethanesulfonyl)imidate appeared as a weakly coordinating counter anion (weaker then OTf^- or ClO_4^-)[45] that formed highly electrodeficient gold cationic complexes (**30**), which appeared to be an air stable gold(I) catalyst. The assumption of stability is based on the observation of stability of $AgNTf_2$ compared to hygroscopic salts AgOTf, $AgBF_4$, $AgPF_6$ and $AgSbF_6$. The simple method of the preparation of **30** (treatment of $(Ph_3P)AuCl$ with 1 equivalent of $AgNTf_2$, which is commercially available, in CH_2Cl_2 at room temperature) and its stability makes the gold catalyst very valuable. As a model substrate, the simple enyne **31** was chosen.



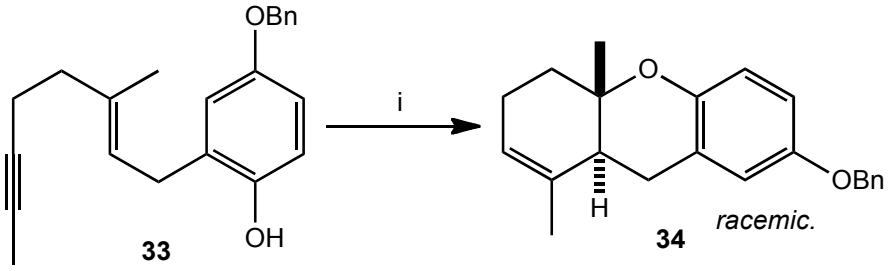
Reagents : i) a) $Ph_3PAuNTf_2$ (**30**) (1 %mol), 5 min., CH_2Cl_2, 97%
b) $Ph_3PAuNTf_2$ (**30**) (0.01 %mol), 30 min., CH_2Cl_2, 97%

Scheme 13

The gold catalyst appeared to be extremely active at room temperature or below.

Complex **30** catalysed the Conia-ene rearrangement, Rautenstrauch rearrangement, and the propargyl Claisen rearrangement previously reported by Toste group in 2004,[43] it was found to be a more efficient catalyst, increasing yields and decreasing the time of the reactions.[44]

The intramolecular phenoxycyclization reaction on 1,5-enyne was reported by Michelet.[46] The group discovered after the investigation of the various Brönsted or Lewis acid catalysts on model substrate **33** that the cationic gold(I) compound $Ph_3PAuNTf_2$ (**30**) (reported by Gagosz) allowed full conversion in 1h at room temperature to product **34** (Scheme 14). The reaction can be prepared in variety of solvents including diethyl ether, toluene or CH_2Cl_2.

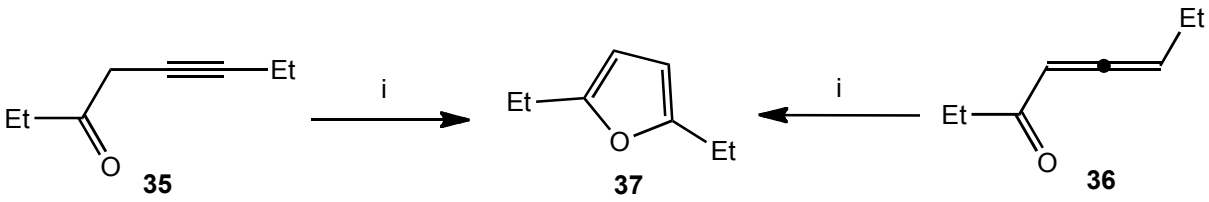


Reagents : i) **30** (1 mol%), solvent, R.T.

Scheme 14

The mechanism of the reaction goes through an initial η^2 coordination of cationic gold(I) to alkyne fragment followed a double-cyclisation process. The *6-endo* mode has been observed.

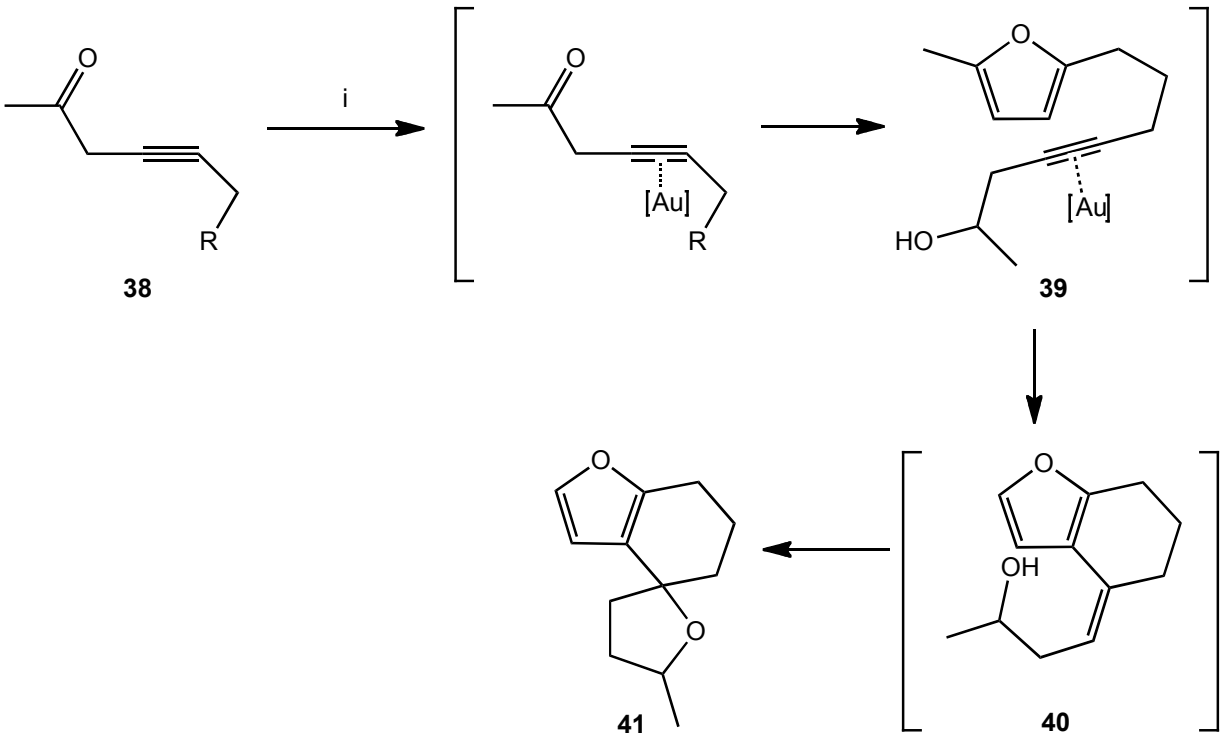
Hashmi tested activity of Au(III) catalysts which include a Pd(II)-like d^8-system.[47] They tried $AuCl_3$ in the reaction with propargyl ketone (**35**) and allene ketone (**36**) to form furan (**37**) in an essentially quantitative yield (Scheme 15).



Reagents : i) $AuCl_3$ (0.1 mol%), CH_3CN.

Scheme 15

In these reactions, no intermolecular C-C bond formation was possible, however with compound **38** (Scheme 16), intramolecular hydroarylation of an alkyne occurred, followed by an intramolecular addition of a hydroxyl group to alkene **38** to **41** via **39** and **40** (Scheme 16).[47]

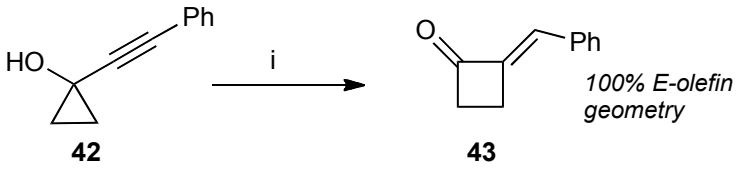


Reagents : i) $AuCl_3$ (0.1 mol%), CH_3CN.

Scheme 16

1.3.2.7 Ring Expansion

The ring expansion is one of the methods of preparation for cyclic ketones.[48,49] Toste in 2005, based on the proposed mechanism that gold(I) can coordinate to an unsaturated C-C bond by introducing *trans*-addition to tethered nucleophile,[35] hypothesised that gold(I) should catalyses the migration of nucleophilic C-C σ-bond.[50] Using 1 mol% $(PPh_3)AuSbF_3$ with alkynylcyclopropanol **42** the alkylidenecyclobutanone **43** was achieved in 95% yield as a single isomer (Scheme 17). Further investigation showed that when an electron-deficient arylophosphines were used as an L ligand, the time of the reaction decreased and yield was improved (Scheme 17). The opposite result were obtained when electron-rich arylophosphine were used (Scheme 17). Echevarren corroborated this observation in 2011 during the investigation of cyclopropanation of alkenes with 1,6-enynes.[51] The follow order of increasing electrophilicity in cationic gold(I) complexes was shown: N-heterocyclic carbine < phosphine < phosphite with SbF_6 as a counterion.

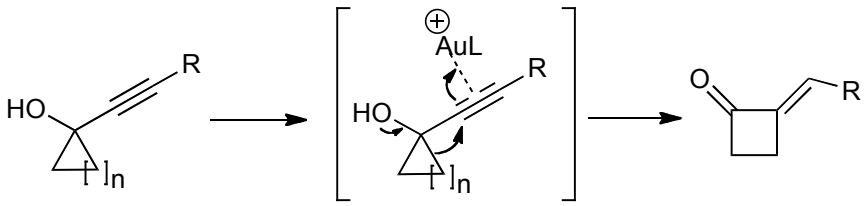


L = PPh_3	95% in 115 min.
L = $(4\text{-}ClC_6H_4)_3P$	97% in 85 min.
L = $(4\text{-}F_3CC_6H_4)_3P$	99% in 25 min.
L = $(MeOC_6H_4)_3P$	90% in 160 min.

Reagents : (i) 1 mol% LAuCl, 1 mol% $AgSbF_6$ CH_2Cl_2, R.T.

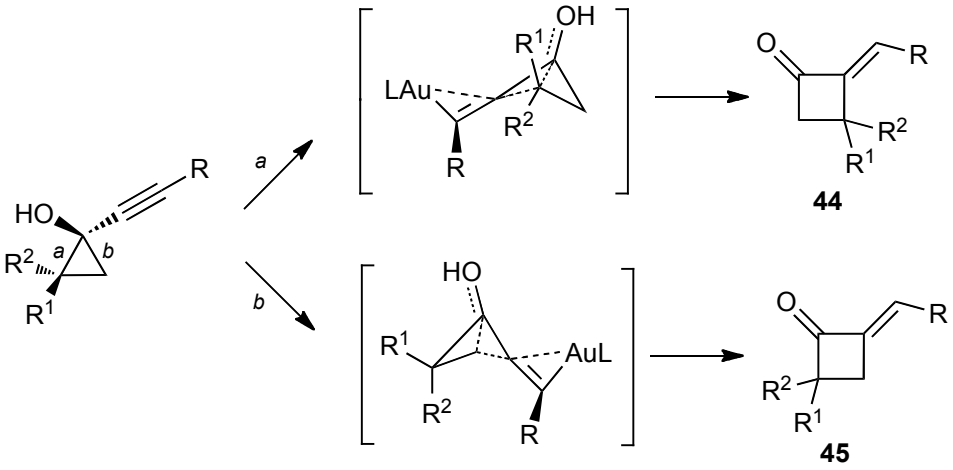
Scheme 17

Authors examined the scope of cyclopropanols and cyclobutanols with tris-(4-trifluoromethylphenyl)phosphine gold(I) catalyst and achieved appropriate products with good to excellent yield.



Scheme 18

The mechanistic hypothesis, supported by selective migration of more substituted cycloalkanol carbons and geometry of olefins, involved cationic gold(I) coordination to alkyne following 1,2-alkyl shift (Scheme 18), however the size of alkynyl substituent influences the geometry of the product due to 1,3 strain between R^1 and R, and R^2 and R groups (Scheme 19).



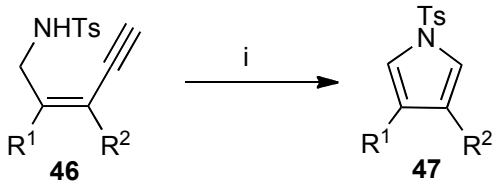
a) R = H, R^1 = ^{i}Pr, R^2 = H 80% only **44**
b) R = Ph, R^1 = ^{i}Pr, R^2 = H 82% **44:45** 4.6:1
c) R = Ph, R^1 = H, R^2 = ^{i}Pr 91% only **45**
d) R = H, R^1 = H, R^2 = Bn 88% **44:45** 1.7:1

Scheme 19

1.3.3 C-N Bond Formation

1.3.3.1 aza-Claisen-Type Rearrangement

Gagosz reported the synthesis of functionalised pyrroles using gold(I) catalyst. Based on Fürstner work on rearrangement of allyl pentynyl ether using $PtCl_2$,[52,53] Gagosz envisaged, that this kind of transformation can be realised with this air-stable $Ph_3PAuNTf_2$ catalyst.[44] The first attempt with compound **46** rapidly achieved expected product **47** with excellent yield in 5 minutes (Scheme 20).

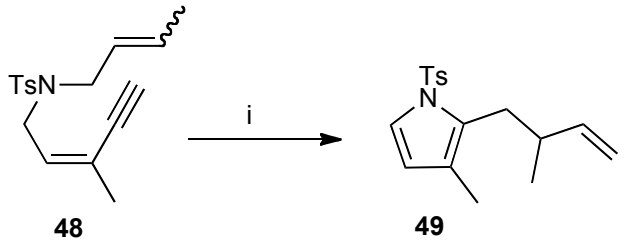


R^1 = H, Cl
R^2 = Me, Ph

Reagents : (i) 1 mol% $Ph_3PAuNTf_2$, CH_2Cl_2, R.T.

Scheme 20

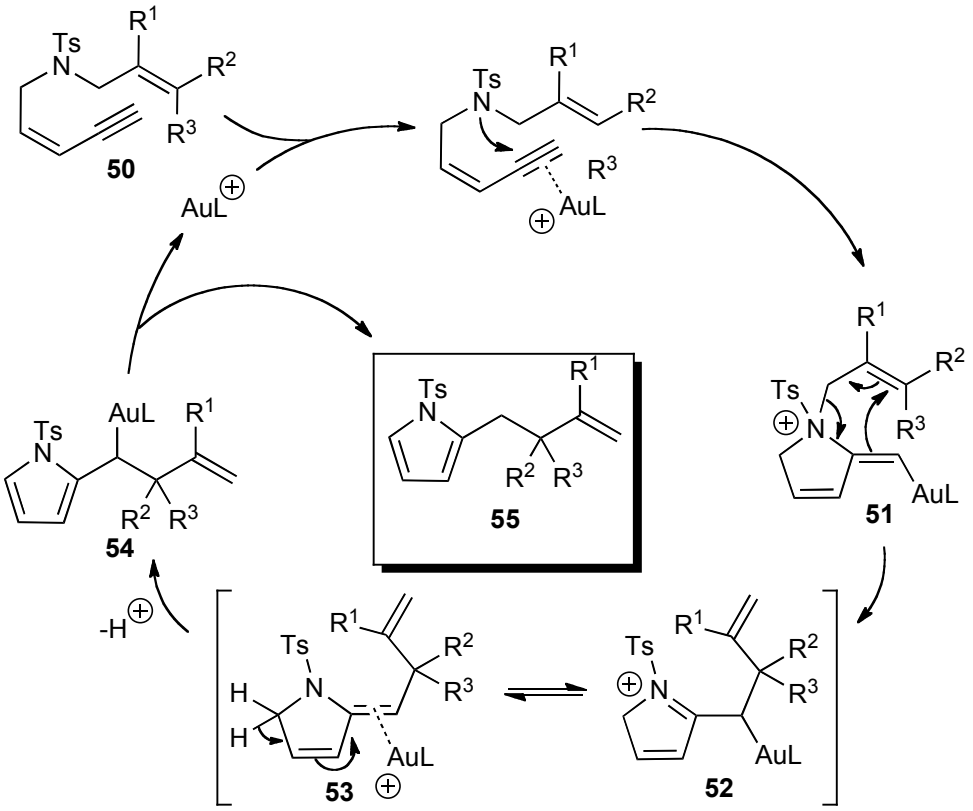
The more challenging compound appeared allyl tosylamide **48** (Scheme 21). In the previously used condition, the cyclisation reaction took 6h in 62% yield of compound **49**. Further investigation provided that more electrophilic substituents (*p*-CF_3Ph-) on phosphine were necessary to increase speed and yield of reaction.



Reagents : (i) 2 mol% (*p*-CF_3Ph)$_3$PAuNTf$_2$, CH_2Cl_2, R.T.

Scheme 21

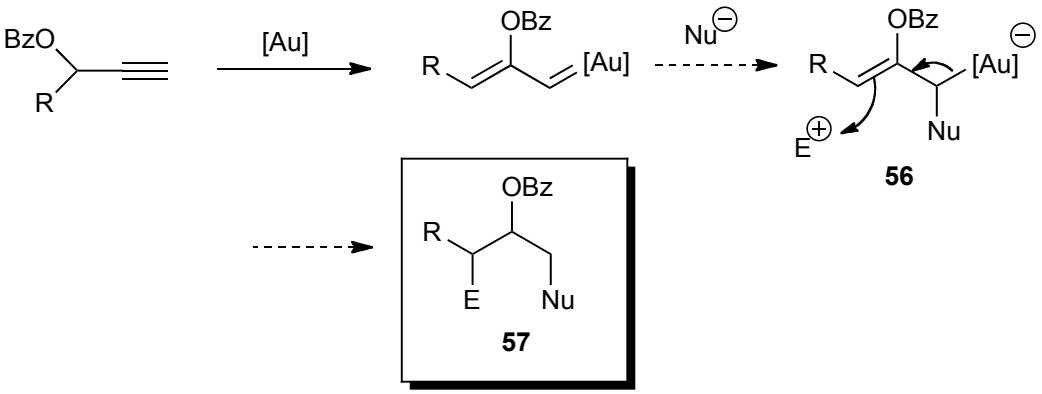
The proposed mechanism of the reaction started with the activation of the triple bond of the allyl tosylamide **50** (Scheme 22) followed by nucleophilic addition of tosylamide. The aza-Claisen rearrangement of compound **51** leads to intermediate **52,** which is presumably in equilibrium with gold (I) complex **53**. The aromatisation occurs after loss of the proton from one of the two intermediates, which yielded the new gold intermediate **54**. Protodemetalated step gave product **55**.



Scheme 22

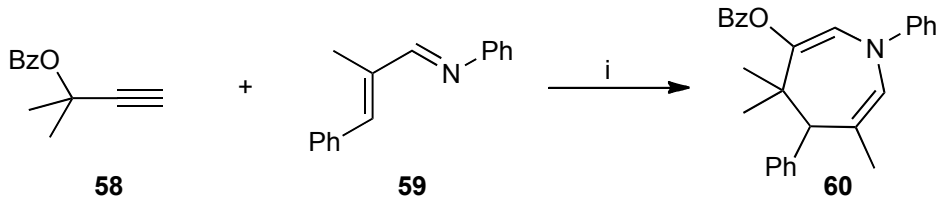
1.3.3.2 Intramolecular [4+3] and [3+3]-Annulation

Toste presented the synthesis of azepines through an intramolecular [4+3] annulation reaction.[54] They postulated that allyl gold intermediate **56** generated by the addition of a nucleophile could further react with an electrophile giving the desired product **57** (Scheme 23).



Scheme 23

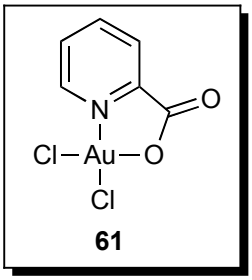
Using a nucleophilic diene, such us α,β-unsaturated imine results in the formation of a new ring. The α,β-unsaturated imine interacts with gold carbenoid (formed with propargyl ester) as a nucleophile. The new established gold intermediate forming in the same time the electrophilic end of α,β-unsaturated iminium. The intramolecular nucleophilic addition to iminium electrophile leads to formation the azepines. The propargyl ester **58** and *N*-phenyl imine **59** (Scheme 24) were chosen and the reaction initially conducted using 10 mol% Ph_3PAuCl and $AgSbF_6$. However only traces of azepine **60** were isolated. A detailed evaluations of different gold compounds (N-heterocyclic carbene IMesAuCl + $AgSbF_6$, AuCl, $AuCl_3$) showed the best catalyst based on the picolinic acid derivative **61** (Scheme 24), which yielded 65% of one desired seven membered ring **60**.



58 **59** **60**

$Ph_3PAuCl + AgSbF_6$	6% yield
AuCl	44% yield
$AuCl_3$	33% yield
$PicAuCl_2$ (**61**) (5%)	65% yield

Reagents: i) 10% catalyst, CD_2Cl_2, R.T.

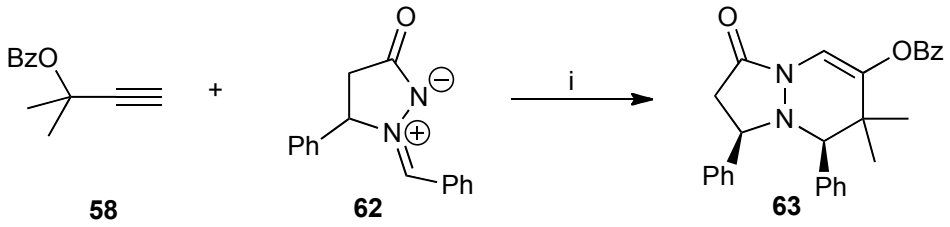


61

Scheme 24

The scope of the propargyl esters (secondary benzylic propargyl esters, tertiary propargyl esters, *tert*-butylcyclohexanone derived ester) was examined and which ones gave good to excellent yield. The indole derivative and quinolone derivative with tertiary propargyl ester were attempted to synthesise in 61% and 93% yield respectively.

In 2009 Toste also reported a [3+3]-cycloaddition of propargyl esters and azomethine imines using the same gold(III) catalysis condition (catalyst based on picolinic acid derivative **61** ($PicAuCl_2$) (Scheme 24))[55] successfully applied in the synthesis of azepines through intramolecular [4+3] annulation reaction.[54] However good yield was also obtained with $AuCl_3$ and $NaAuCl_4$. The use of gold(I)-catalyst prepared *in situ* from Ph_3PAuCl and $AgSbF_6$ appeared to be not compatible with this reaction. Biscyclic [3+3] cycloadduct **63** was synthesised from the ylide **62** and propargyl ester **58** in a 90% yield and 6:1 *cis*:*trans* diastereoselectivity at room temperature (Scheme 25).

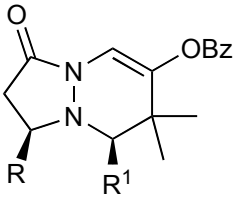


58 **62** **63**

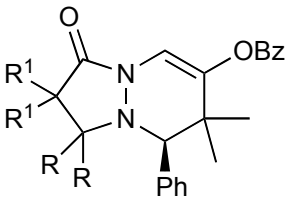
Reagents: (i) 5% catalyst, CD_2Cl_2, R.T.

Scheme 25

Altering the solvents in the reaction from non-polar (benzene) to semi-polar (dichloromethane) and polar (acetonitrile, nitromethane) led to significant changes for both the yield and the selectivity, with the best being achieved by using dichloromethane. The best diastereoselectivity 8:1 *cis*:*trans* researchers achieved at 0 °C. Using these conditions, a range of different substituted ylides were examined and obtained very good yield as depicted on the Scheme 26.



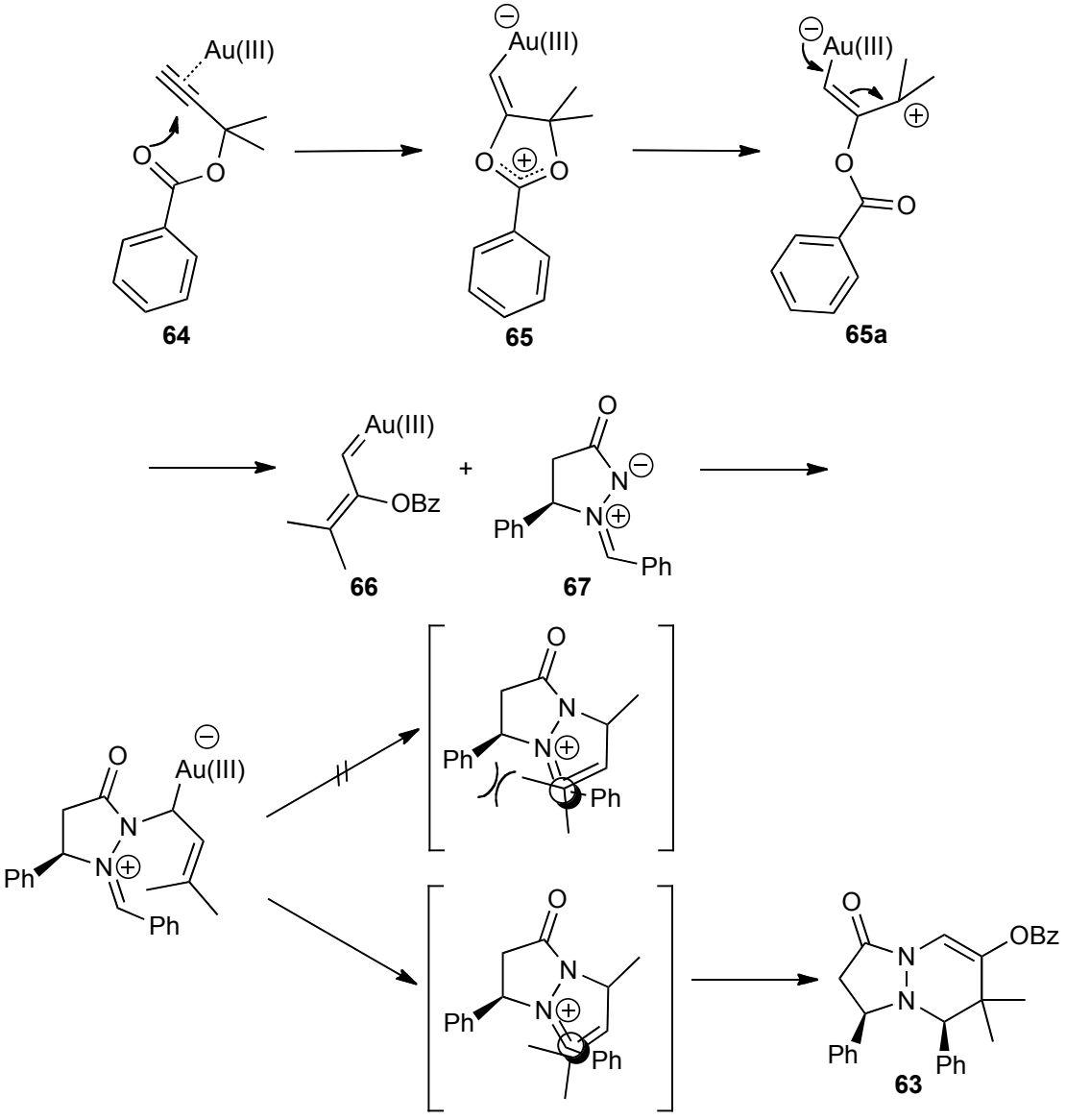
1) R = Ph, R^1 = 3,4,5-$(MeO)_3C_6H_2$ — 80% (6 : 1) *cis*:*trans*
2) R = Ph, R^1 = 4-CN-C_6H_4 — 94% (5 : 1) *cis*:*trans*
3) R = Me, R^1 = 3-piridyl-2-Cl — 98% (1.7 : 1) *cis*:*trans*
4) R = Me, R^1 = 2-I-C_6H_4 — 72% (1.8 : 1) *cis*:*trans*
5) R = Ph, R^1 = cyclopropyl — 41% (2.8 : 1) *cis*:*trans* R.T.



6) R = Me, R^1 = H — 82% R.T.
7) R = H, R^1 = Me — 88% R.T.

Scheme 26

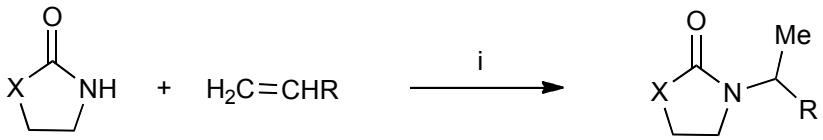
The authors did not suggest a mechanism for the whole reaction but it presumably proceeds *via* the complexation of the triple bond to **64** followed by rearrangement through the transition species **65** and **65a** giving a metal-carbenoid **66**. The cyclisation of 1,3-dipole **67** with metal-carbenoid species **66** then yields the desired product **63** (Scheme 27). The diastereoselectivity of the reaction was rationalised by unfavourable steric interaction between the allyl methyl group of the chain and β-substituent during the ring closing state (Scheme 27).



Scheme 27

1.3.3.3 Intermolecular Hydroamination Reaction

Based on his previous work on intramolecular hydroamination of γ- and δ-alkenyl ureas at room temperature,[56] in 2009 Widenhoefer reported an intermolecular Markovnikov-selective gold(I) hydroamination reaction of ethylene and 1-alkenes with cyclic ureas.[57] The reaction was performed at 100 °C in dioxane at 120 psi (8.27 bars) alkenes in presence of 5% (2-biphenyl)di-tert-butylphosphine gold chloride (**68**) with 5% silver trifluoromethanesulfonate (AgOTf). A number of cyclic ureas and different alkenes were used successful (Scheme 28, Table 2). The alkenes with hydroxyl, benzoxyl, carboxylic acid and carboxylic acid ester groups were converted to product with very good to excellent yield (Scheme 28, Table 2).



Reagents: i) 5 mol% **68**, 5 mol% AgOTf, dioxane, 100 °C.

Scheme 28

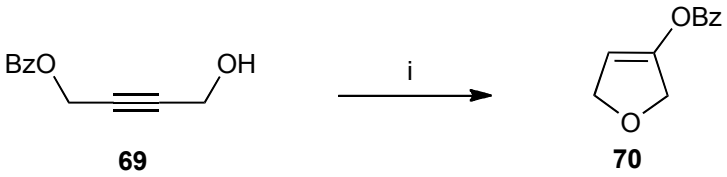
Table 2

Entry	Nucleophile X =	Alkene R=	Time [h]	Yield %
1	NMe	H	20	99
2	NMe	Et	69	99
3	N*t*-Bu	H	40	80
4	NMe	$(CH_2)_3OH$	24	98
5	NMe	$(CH_2)_3OBn$	40	95
6	NMe	$(CH_2)_2CO_2H$	40	98
7	NMe	$(CH_2)_2CO_2Et$	40	90

1.3.4 C-O Bond Formation

1.3.4.1 Functionalised 2,5-dihydrofurans Formation

In 2001, Krause[58] reported that 2,5-dihydrofurans can be synthesised using α-hydroxyallenes with gold(III) chloride. Four years later Zhang[59] reported 3,3-rearrangement of propargylic esters into allenes using $Ph_3PAuCl/AgSbF_6$. In 2006, Gagosz based on the Krause and Zang works, proposed new way of preparation 2,5-dihydrofurans through a gold-catalysed tandem reaction.[60] Benzyl protected 1,4-*cis*-butynol **69** was chosen as a model substrate and successfully converted to product **70** in 83% yield in over two isomerisation steps a in one pot reaction (Scheme 29) with 1 mol% of $Ph_3PAuNTf_2$.



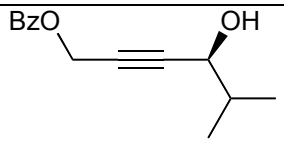
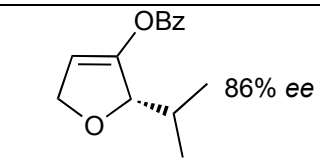
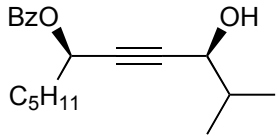
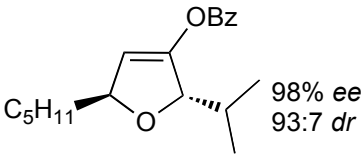
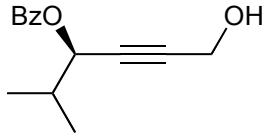
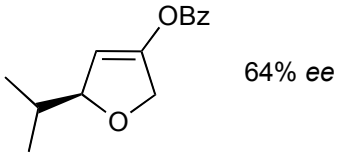
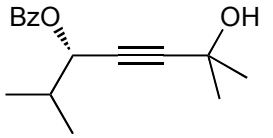
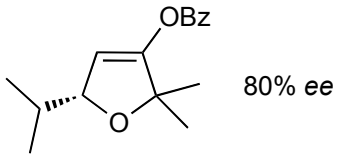
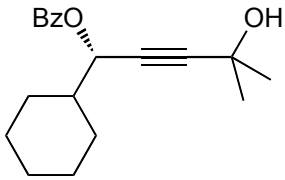
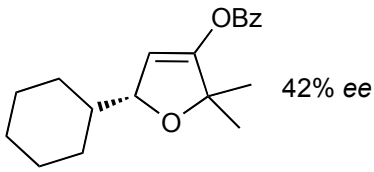
Reagents: i) 1 mol% PPh_3AuNTf_2, CH_2Cl_2, R.T., 83% yield.

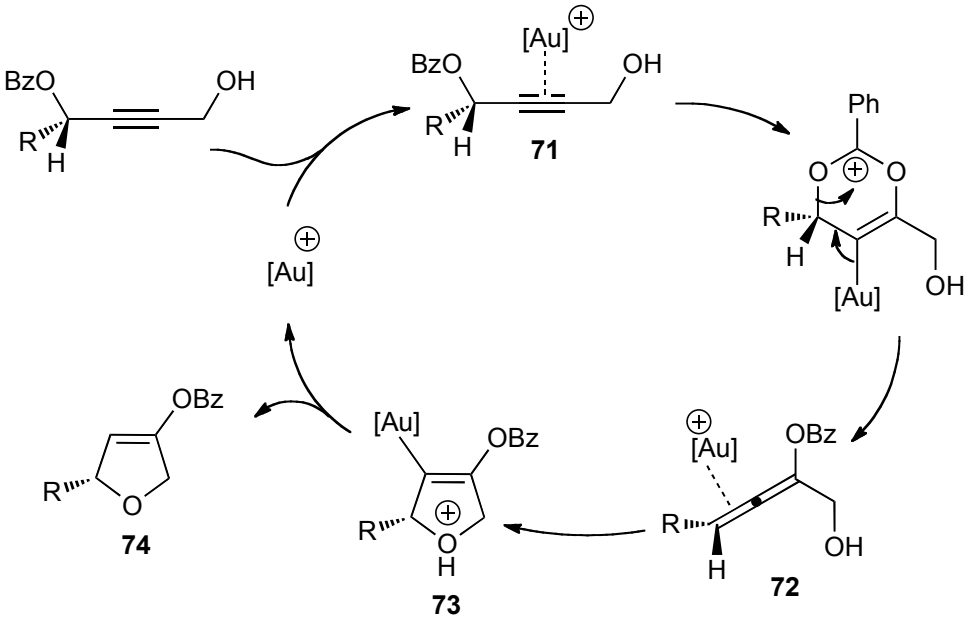
Scheme 29

Mono-, di- and trisubstituted propargylic esters were attempted under standard condition reactions with very good yields (69 to 99% yield). Following these results, the authors synthesised a range of chiral propargyl benzoates derivatives and reacted them with 2 mol% of $Ph_3PAuNTf_2$ (Table 3). In most cases the product maintained the optical purity of the starting material (Entry 1, 2, 4). However in two examples the enantiomeric excess was significantly lower (Entry 3 and 5). This lost of the optical purity appeared to be connected with size of the group attached next to the protected alcohol. The authors suggested that racemisation might be caused by '*competition between a possible gold(I)-catalysed isomerization of intermediate allene and nucleophilic attack of the alcohol onto gold-activated allene*'.[60] The racemisation problem was solved by optimisation of the reaction conditions by changing catalyst. Using 2 mol% of (Ad_2n-BuP)$AuNTf_2$ (Ad = adamantyl) at 0 °C in dichloromethane on the problematic substrates (Entries 3 and 5)

resulted in 99% yield with 90% *ee* and 91% yield with 74% *ee* respectively. The mechanism of the reaction was proposed as starting with the activation of the triple bond in propargyl ester **71** followed by 1,3-shift of the ester group that yielded the allene intermediate **72**. The regenerated gold(I)-catalyst activates the terminal double bond of the allene prompting the intramolecular nucleophilic attack of the alcohol group. The resulting vinyl-gold intermediate **73** is then finally protonated to yield 2,5-dihydrofuran **74** (Scheme 30).

Table 3

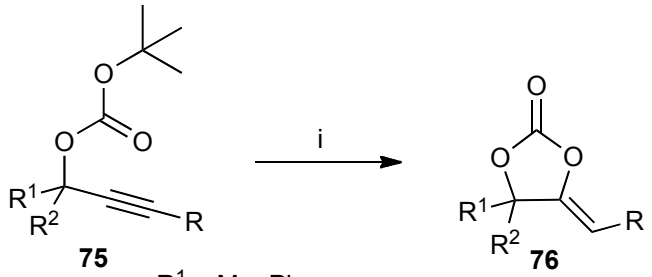
Entry	Substrate	Product	Time	Yield %
1	 87% *ee*	 86% *ee*	3h	83
2	 98% *ee* 93:7 *dr*	 98% *ee* 93:7 *dr*	40 min.	97
3	 96% *ee*	 64% *ee*	15 min.	99
4	 81% *ee*	 80% *ee*	50 min.	95
5	 94% *ee*	 42% *ee*	10 min.	89



Scheme 30

1.3.4.2 Dioxolones, Oxazolidineones and Oxazolones Formation

Gagosz, based on his work on the gold-catalysed synthesis with $Ph_3PAuNTf_2$ of the 4-alkylidene-1,3-dioxolones **75** from propargylic *tert*-butly carbonates **76** (Scheme 31)[61] postulated that propargyl *tert*-butyl carbamate **77** could provide the corresponding 5-methylene-1,3-oxazolidine-2-one **78** in an analogous cyclisation reaction (Scheme 32).[62]

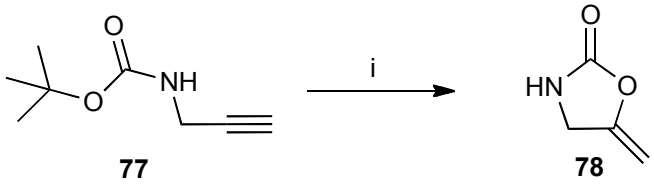


R^1 = Me, Ph
R^2 = Me, Et
R^1-R^2 = - $(CH_2)_5$ -
R = Br, CO_2Et, $-CH_2OBoc$

Reagents: i) 1 mol% PPh_3AuNTf_2, CH_2Cl_2, R.T.

Scheme 31

The first attempt with substrate **77** (Scheme 32) gave the expected oxazolidinone **78** in only 37% yield after 1 hour, when corresponding propargylic *tert*-butly carbonates reached 83% yield after only 10 minutes. Increasing the duration or equivalent of catalyst did not affect the yield, even after 72 hours with 3 mol% of catalyst, the yield only reached 44% (Scheme 32).



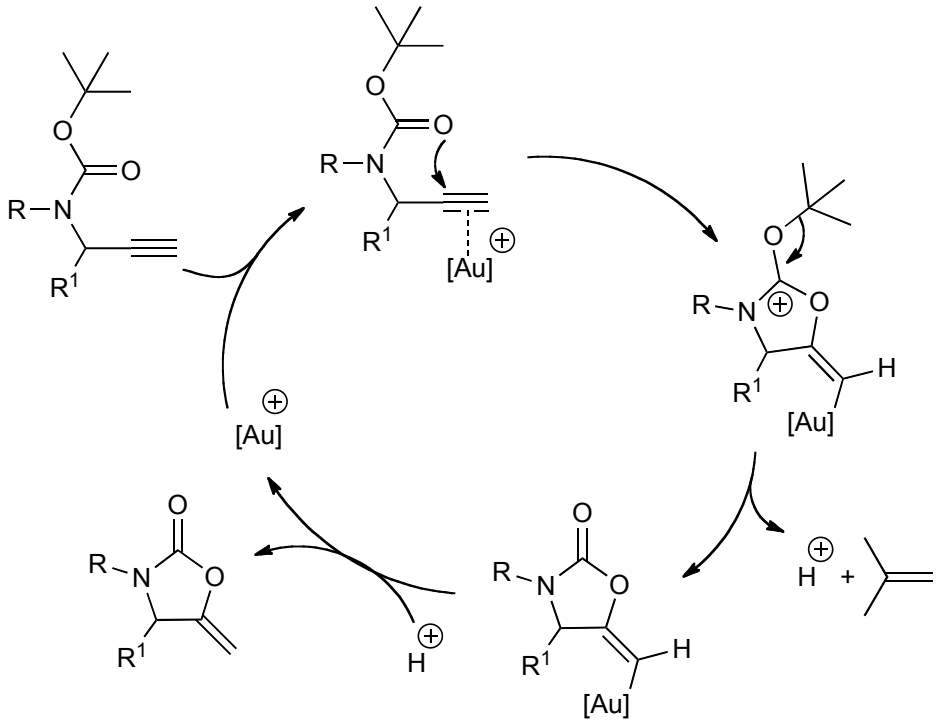
77 **78**

1)	n = 1	1 h, R.T.	37%
2)	n = 1	24 h, R.T.	44%
3)	n = 1	2 h, reflux	40%
4)	n = 3	72 h, R.T.	44%

Reagents: i) n mol% PPh_3AuNTf_2, CH_2Cl_2, R.T.

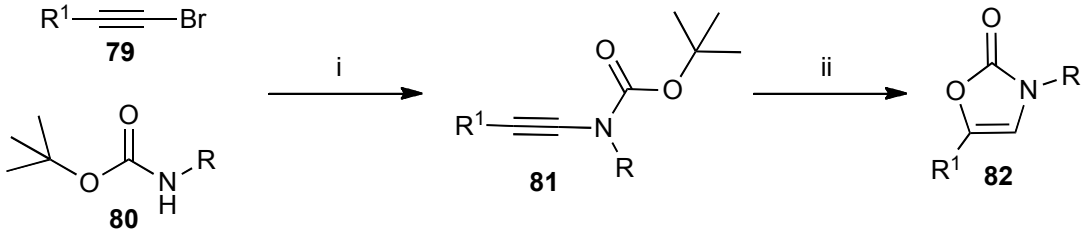
Scheme 32

The cause of the problem might be due to equilibrium between the two possible rotamers. Simple replacement the benzyl group to nitrogen solves the problem and corresponding product was obtained in 98% yield. Another solution was the substitution of the propargyl position by two methyl groups (Thorpe-Ingold effect[63]- gem-dimethyl effect or angle compression, the increased size of the substituents on tetrahedral center increases the angle between them and the angel of other two substituents moved closer together which accelerate reaction between them). This resulted in the formation of product in 30 minutes in a 99% yield. Many different substituted (propargyl position: aryl groups possessing electron-withdrawing group or electron-donating group; nitrogen position: Bn, Ph, cyclopropyl, cyclobutyl, propargyl) products were synthesised with good to excellent yields (65 to 100%). The postulated mechanism of the reaction is showed on Scheme 33.



Scheme 33

In 2008 Gagosz presented a two step sequence for the formation of 1,5-disubstituted oxazolones.[64] The first step was the coupling of bromoalkyne **79** with *tert*-butoxycarbamate **80** performed in the presence of 20 mol% $CuSO_4 \cdot 5H_2O$, 10% of 1,10-phenantroline as a ligand and K_3PO_4 as a base, to prepare starting material *N*-alkynyl *tert*-butyloxycarbamates **81**. The second step of the sequence using $Ph_3PAuNTf_2$ gave poor result (28% yield), even more electrophilic $pCF_3Ph_3PAuNTf_3$ improved yield to 52% at room temperature. Optimisation of the 5-*endo*-trig cyclisation showed that the best yield could be obtained using 1 mol% $[(Ph_3P)Au(NCMe)]^+ SbF_6^-$ at 40 °C, giving the desired oxazolones **82** (Scheme 34) in 74% yield where R = C_5H_{11} and R^1 = Ph.



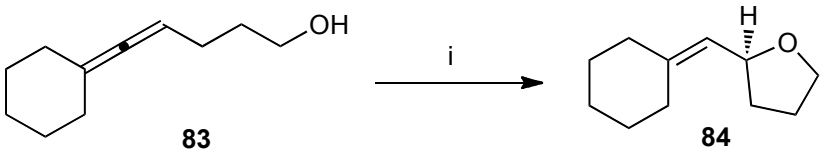
Scheme 34

Further *N*-alkynyl *tert*-butyloxycarbamates was synthesised containing various functionalities (R^1 = Ph, *t*-Bu, *n*-C_5H_{11}, CH_2OAc, 1-cyclohexene; R = 4-fluorocyclohexane, 4-chlorocyclohexane, 4-bromocyclohexane, Bn, 2,4-dimethoxybenzene, naphthalene, silyl ether) and used in cyclisation reaction. The similar mechanism was proposed as shown above; containing triple bond activation followed cyclisation with isobutene migration that furnished a vinyl-gold species. Protodemetalated step gave the appropriate oxazolones.

1.4 Known Enantioselective Transformations Catalysed by Gold

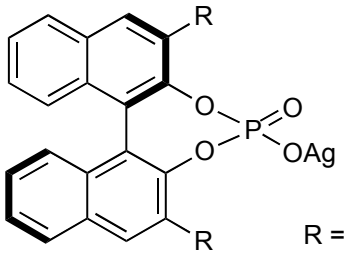
1.4.1 Chiral counterion strategy (X ligand)

Traditional enantioselective transition metal catalysis is based on chiral ligand, being tightly attached *via* covalent bond to metals – the reactive side of catalyst. Arndtsen,[65] based on evidence that non coordinating or weakly coordinating counterions can influence the selectivity in metal-catalysed reactions, suggested that '*significant ionic interaction can occur during catalysis*'[65] with the result, that chirality can be inducted in the product using catalyst which associated with chiral counterion.[65] His work on copper catalysis included the first examples of metal-catalysis, where asymmetry was induced by chiral counterion containing two binaphtyl molecules bonded to a tetrahedral boron centre (in a styrene aziridination reaction). The authors found that a strong ion-paring between metal and counterion existed in nonpolar solvents such as benzene which gave higher enantiomeric excess. When polar solvents such as acetonitrile were used, the result was almost total lost of enantiomeric purity. Based on this knowledge in 2007 Hamilton, Kang, Mba and Toste showed this alternative approach in gold catalysis.[66] When the catalyst was with chiral phosphine ligand, the chemists found the hydroalkoxylation reaction of allenes as difficult to achieve with broad scope of products and with high enantioselectivity.[67] The catalyst was prepared *in situ* by treatment of 2.5 mol% of dppm$(AuCl)_2$ with 5 mol% silver phosphate **85** in the presence of allene **83** (Scheme 35) in dichloromethane. The product **84** (Scheme 35) was obtained in 76% yield and 65% enantiomeric excess. Further investigation of the solvent confirmed Arndtsen's ion-pair model, with benzene giving the best results (Table 4).



Reagents : i) dppm$(AuCl)_2$, DCM.

dppm = Ph_2P Ph_2P



85

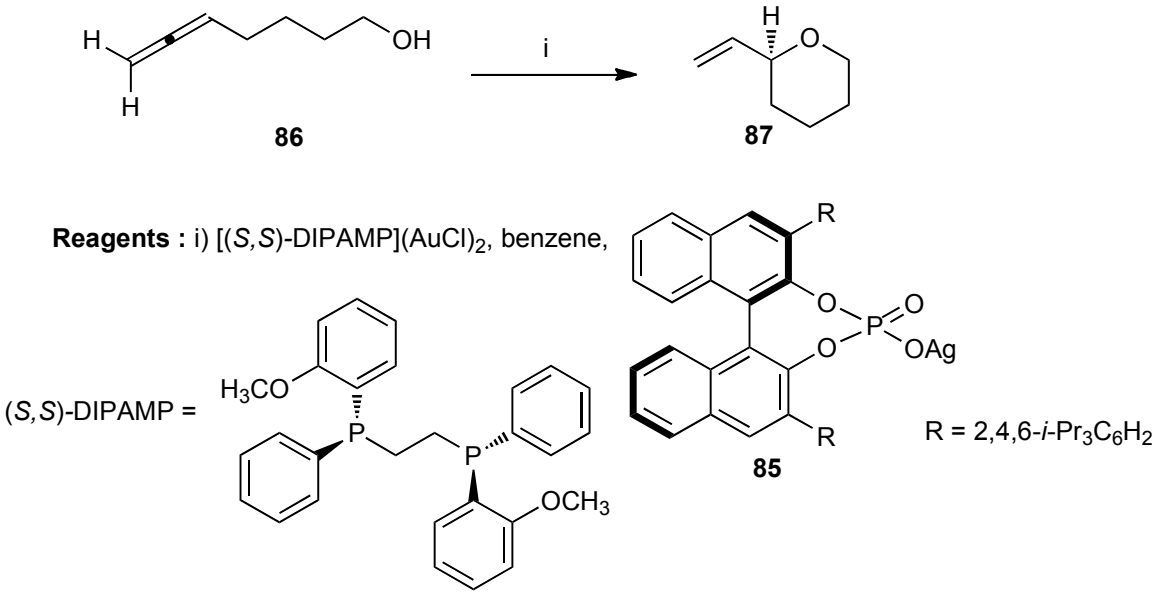
R = 2,4,6-*i*-$Pr_3C_6H_2$

Scheme 35

Table 4

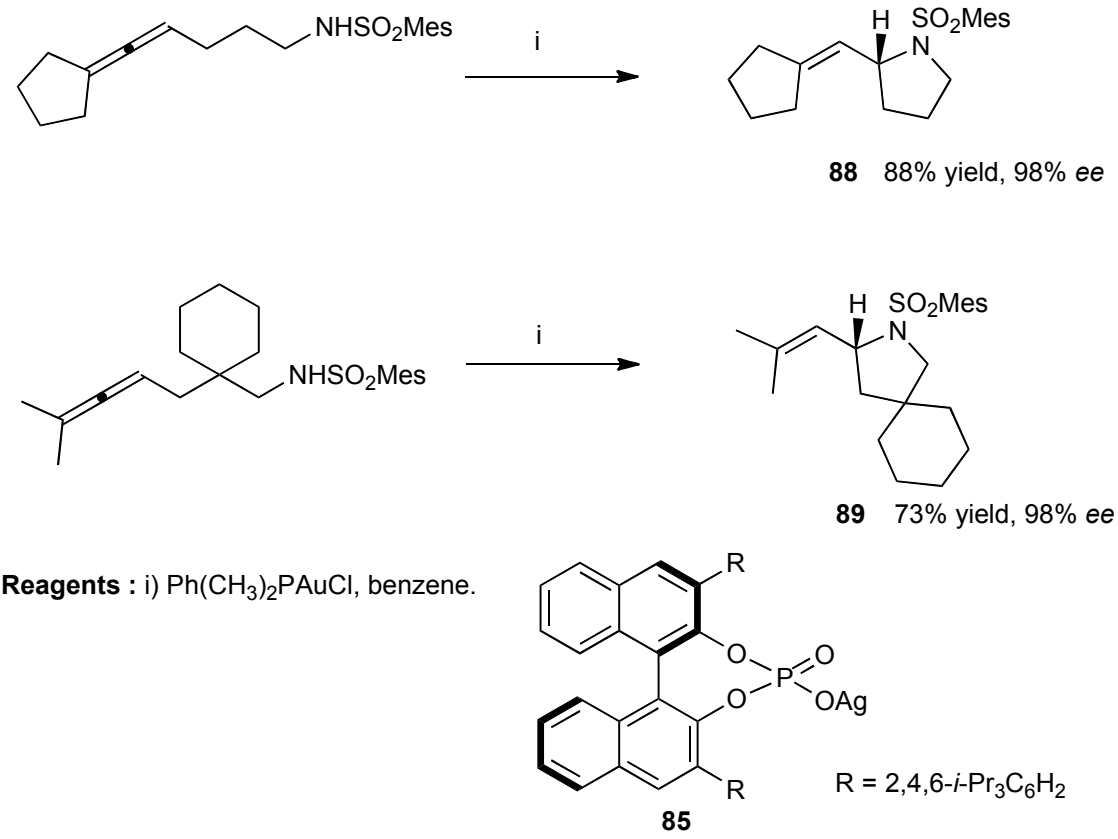
Entry	Solvent	Yield %	*ee %*
1.	CH_3NO_2	60	18
2.	acetone	71	37
3.	THF	83	76
4.	benzene	90	97

The range of different substituted substrates was investigated and well tolerated including substituent in α and β position and terminus allene. In next step authors combined chiral ligand [(*S,S*)-DPAMP]$(AuCl)_2$ and (*S*)-chiral silver phosphate counterion (**85**). The new system was investigated with substrate **86**, giving cyclic ether **87** in 96% yield and 92% enantiomeric excess. By comparison previous method gave the same yield but only in 80% enantiomeric excess (Scheme 36). The new system appeared to be a very powerful catalyst with good enantioinduction.



Scheme 36

The hydroamination reaction of allenes were also attented using the chiral counterion strategy by Toste.[66] Using cationic gold(I) with phenyldimethylphosphine as a L-ligand with chiral phosphate counterion in benzene, achieved transformation of a numbers of allene-sulfonamides bearing different substituents. The scope of pyrrolidine product was obtained with good yields and high level of enantioselecivity (generally above 96% enantiomeric excess) (Scheme 37). Authors reported higher enantiomeric excess in two examples which were previously reported by their own (**88** 75% yield, 83% *ee*; **89** 99% yield, 70% *ee* respectively), using (*R*)-xylyl-BINAP(AuOPNB)$_2$ (where OPNB = *p*-nitrobenzoate).[68]

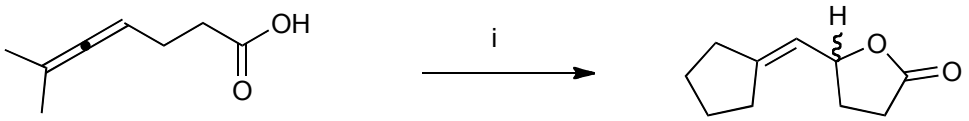


Scheme 37

The mechanism in both cases (hydroalkoxylation and hydroamination) starts from complexation of gold to the internal allenyl C=C bond forming gold-allene complex, followed cyclisation of gold-allene complex with deprotonation/protonolysis.

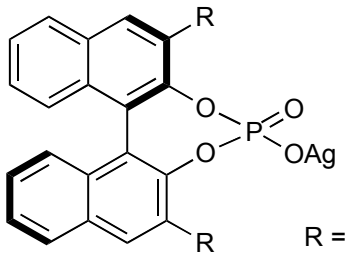
In the same group the asymmetric hydrocarboxylation of allenes was attempted.[66] Disappointing results of enantiomeric excess were obtained using chiral BINAP$(AuCl)_2$ with *p*-nitrobenzoate as counterion (Entry 1, Scheme 38). The poor asymmetric induction was found using dppm$(AuCl)_2$ with chiral counterion **85** (Entry 2, Scheme 38) which was used successfully in hydroalkoxylation reaction.[66] These unsatisfactory results encouraged the authors to use a newly invented catalytic system with a chiral phosphine gold cation, based on BINAP and the previously mentioned chiral phosphate **85**. When the same *R*-enantiomer of phosphine gold cation and phosphate counterion were combined and tested in hydrocarboxylation (previously used successfully, surprisingly the enantiomeric excess was really poor) (Entry 3, Scheme 38). In contrast, when *S*-enantiomer of phosphine gold

cation was used with *R*-enantiomer **85** the enantiomeric excess reached 82% (Entry 4, Scheme 38).



1) L = (*R*)-BINAP X = 4-(NO_2)-C_6H_4-COOAg 80% yield, 38% *ee* (*R*)
2) L = dppm X = (*R*)-**85** 89% yield, 12% *ee* (*S*)
3) L = (*R*)-BINAP X = (*R*)-**85** 91% yield, 3% *ee* (*R*)
4) L = (*S*)-BINAP X = (*R*)-**85** 88% yield, 82% *ee* (*S*)

Reagents : (i) 2.5 mol% $L(AuCl)_2$, 5 mol% X, benzene,



R = 2,4,6-*i*-$Pr_3C_6H_2$

85

Scheme 38

Mikami reported his work on the control of axial chirality in the bis(phosphanyl)biphenyl (BIPHEP) gold complex using the binaphtol-derived phosphate anion in 2009.[69] The thermodynamically disfavoured diastereoisomer of BIPHEP in gold chloride compound was converted to the thermodynamically favoured in acetone at 100 °C with chiral silver binaphtol-derived phosphate (**90**) substituted by *ortho*-disubstituted phenyl ring (Figure 5) with 100% conversion.

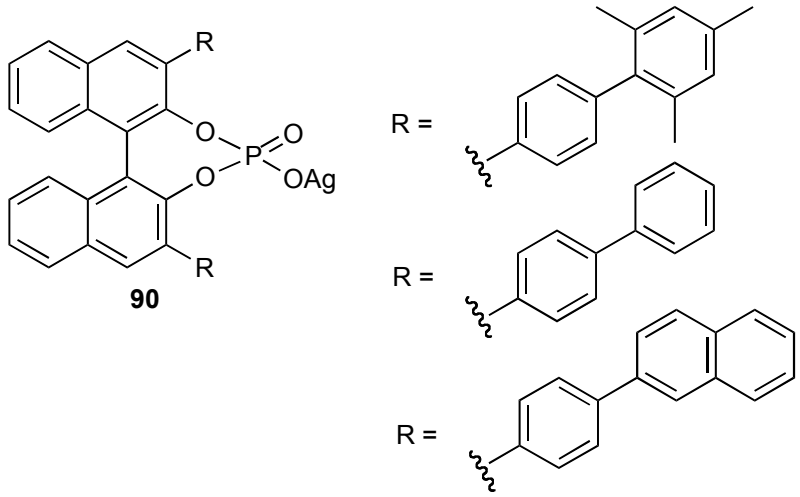
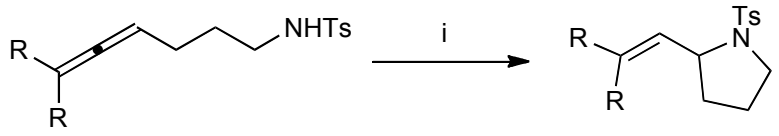


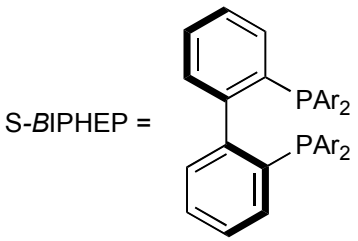
Figure 5

The authors found that concentration had a big influence on the isomerisation as the acetone stabilises cationic intermediate when dissociated from the chiral anion. The pure enantiomeric (*S*)-BIPHEPAuCl was isolated and used successful with hydroamination reaction (Scheme 39). The authors change the couterion from *p*-nitrobenzoate to the previously used binaphtol-derived phosphate (**90**) substituted by *ortho*-disubstituted phenyl ring (the enantiomeric excess was not specified and the investigation was suggested). It was confirmed that even after reaction, epimerisation of BIPHEP did not occur.



R = CH_3, $-CH_2(CH_2)_2CH_2-$, $-CH_2(CH_2)_3CH_2-$

Reagents : i) 5 mol% *S*-BIPHEP$(AuCl)_2$, 10 mol% *p*-nitrobenzoate, $(CH_2Cl)_2$,



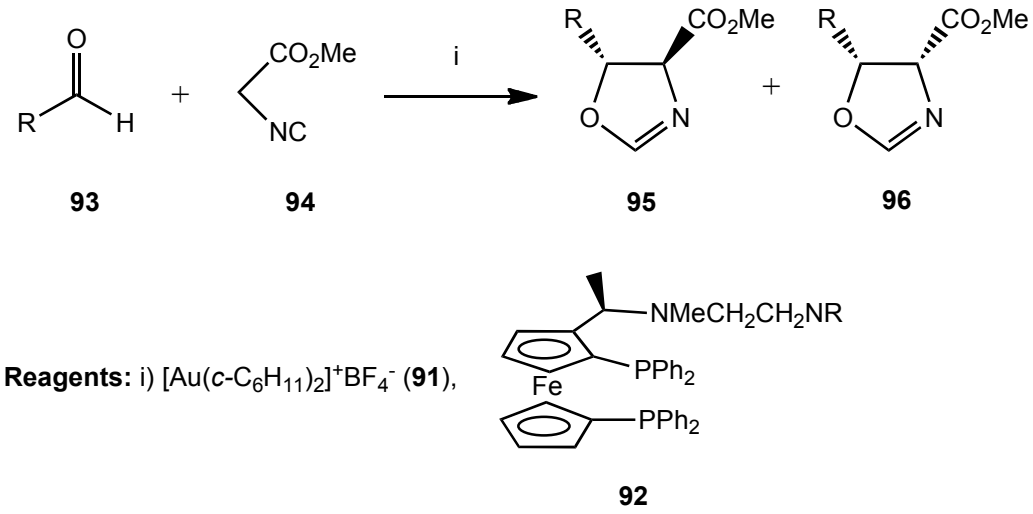
a) Ar = Ph
b) Ar = 3,5-$Me_2C_6H_3$

Scheme 39

1.4.2 Atropisomerism as a source of chirality (L ligand)

1.4.2.1 Carbonyl Group Activation - Asymmetric aldol condensation - Ferrocenyl Ligand

In 1986 Hayashi and Ito reported the first asymmetric aldol condensation reaction catalysed by a gold complex containing both planar and central chirality.[70] They found that the gold complex (0.01 mol%) generated *in situ* by mixing gold compound (**91**) with chiral ferrocenyly phosphine (**92**) gave effective catalysis with a variety of aldehydes (**93**) and methyl isocyanoacetate (**94**) (Scheme 40). The reaction was carried out in dry dichloromethane under nitrogen with the *trans*-compound (**95**) (Scheme 40) obtained as the major product and in high enantioselectivity (>90% enantiomeric excess).



Scheme 40

They postulated a structure for the catalyst-substrate complex in which the side chain participated in the formation of the enolate of the isocyanoacetate, coordinated with gold (Figure 6). The amine group of the ligand was essential for achieving high enantioselectivity in reaction (the pendant Levis base enforced an organised transition state structure) with cyanoacetate deprotonation.

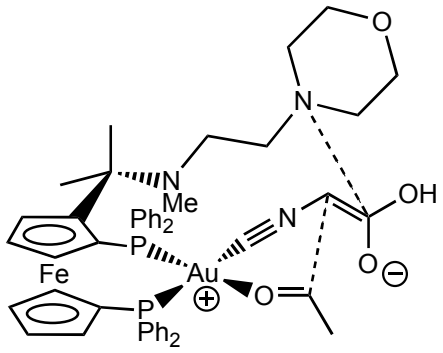
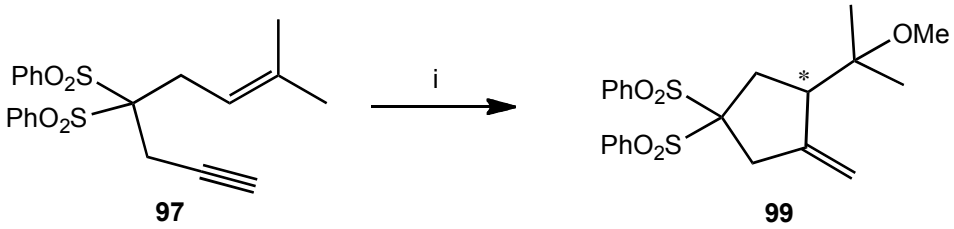


Figure 6

1.4.2.2 Alkyne Activation - Asymmetric Cycloisomersation – Ferrycenyl Ligands, Phosphine Ligands

The first asymmetric alkoxycyclization of 1,6-enyne **97** (Scheme 41) was achieved by Echavarren in 2005.[71]



97 **99**

Reagents : i) 2 mol %[Au(L)Cl] (**98**), MeOH, R.T.

Scheme 41

Several Au(I)-complexes with axially chiral L-ligands based on bidentate phosphines and ferrocennylphosphines were synthesised (**98a-h**) (Figure 7). The reactions were carried out in methanol in the presence of silver salt, $AgSbF_6$ (2-4 mol %) and 1.6-2 mol % of gold chloride pre-catalyst. The absence of a silver salt decreased reactivity and enantioselectivity. The product **99** (Scheme 41) was obtained in excellent yield (84-100%); however the enantiomeric excess was low and the best result did not exceed 53% **98g** (L=(*R*)-TolBINAP) (Table 5). Similar reactivity was observed in Et_2O, acetone, dioxane, and nitromethane with 10 eq. of MeOH. In toluene, DMF, CH_3CN and THF the product **99** was not obtained.

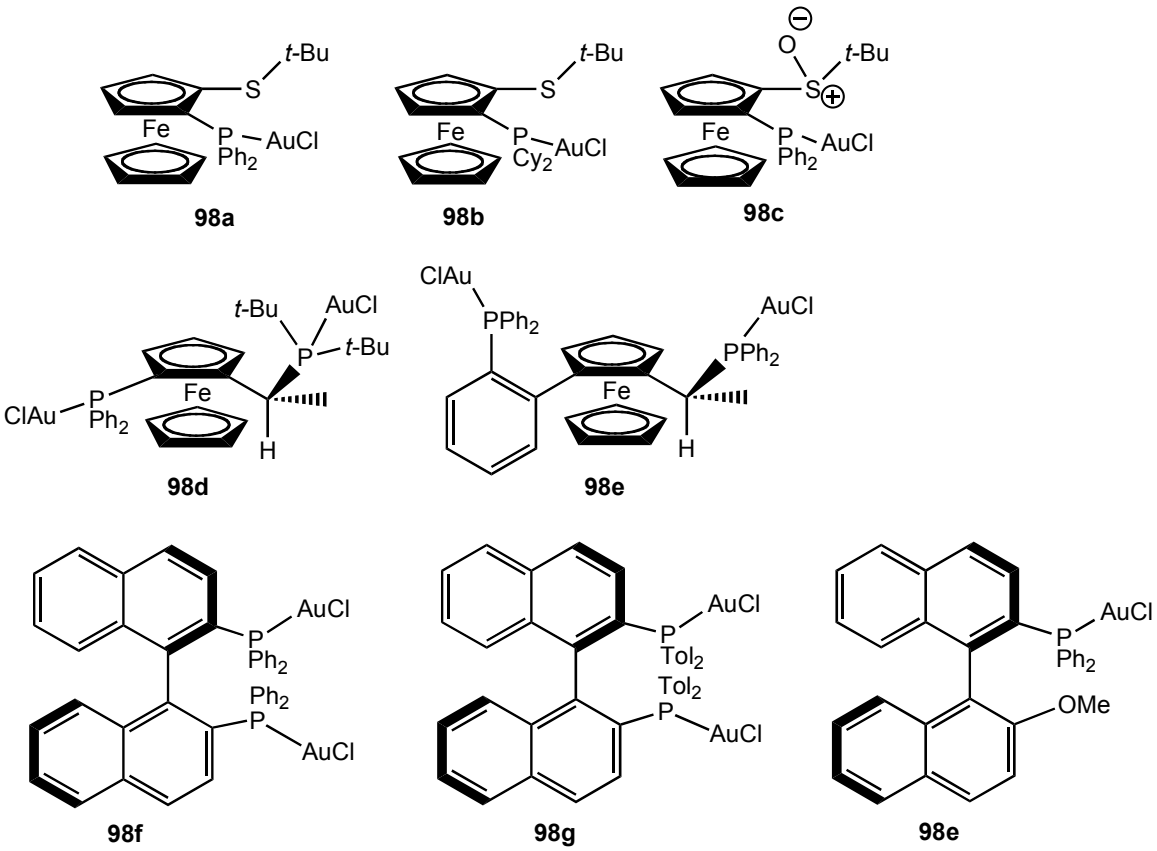
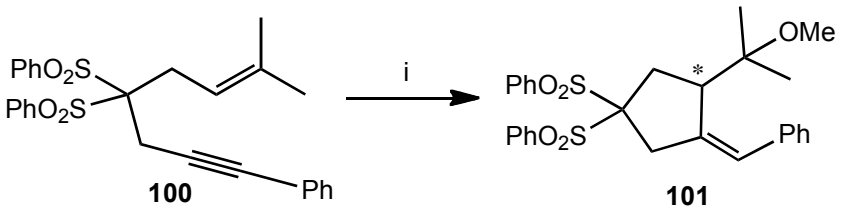


Figure 7

Table 5

Entry	Au(I) complex	Yield [%]	% *ee* (config)
1	**98a**	92	18 (+)
2	**98b**	100	11 (+)
3	**98c**	100	8 (-)
4	**98d**	100	42 (+)
5	**98e**	84	38 (+)
6	**98f**	98	39 (-)
7	**98g**	89	53 (-)
8	**98h**	94	< 2

A good enantiomeric excess (94%) was only reached in one example. In this case, phenyl-substituted enyne **100** was used (Scheme 42) in the presence of (*R*)-TolBINAPAuCl and $AgSbF_6$ (1.6 mol% : 2 mol%), however the yield of product **101** was only 52% after 168 h. This high enantiomeric excess could be a results of the highly crowded cyclopropyl gold(I)-carbene intermediate in 5-*exo-dig* process. The cyclopropyl gold(I)-carbene intermediate was trapped with styrene to give the corresponding cyclopropanes.[72]

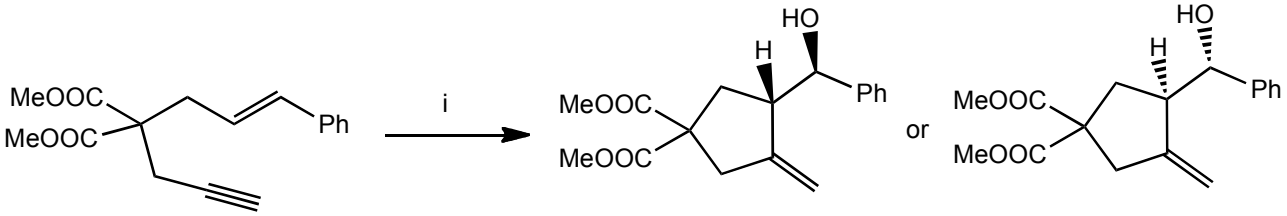


100 **101**

Reagents : i) 1.6 mol (**98g**), MeOH, RT.

Scheme 42

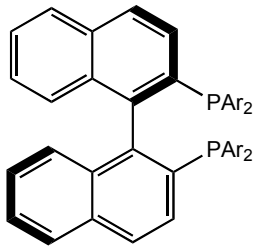
In 2009, Michelet investigated the asymmetric cycloisomerisation of 1,6-enyne using AuCl or $AuCl_3$ both with axial chiral ligand system.[73] The enyne **45** (Scheme 43) was chosen as the starting material. The examination of catalysts showed higher activity with the Au(III) catalyst. The investigation of hydroxycyclisation reaction resulted in the optimal condition being: 10 mol% $AuCl_3$, 30 mol% $AgSbF_6$, and 5 mol% ligand (**103**) at room temperature in dioxane/H_2O. The chiral phosphine ligands (electron-poor as **103i** and electron-rich as **103g**) (Figure 8) were used in conversion of **102** to **104a** or **104b** (Scheme 43) depending on the ligand set.



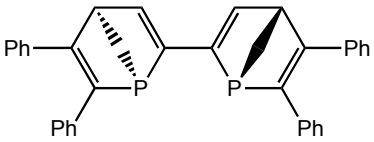
102 **(-) 104a** **(+) 104b**

Reagents : i) 10 mol% $AuCl_3$, 30 mol% $AgSbF_6$, 5 mol% chiral ligand **103**, dioxane/H_2O (6/1).

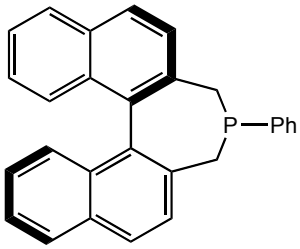
Scheme 43



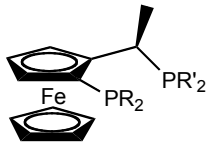
103a Ar = *p*-Me-C_6H_4, ((*R*)TolBINAP)



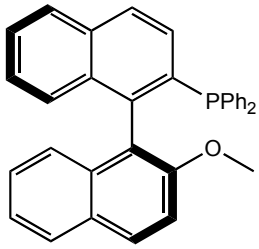
103b (+)-BIPNOR



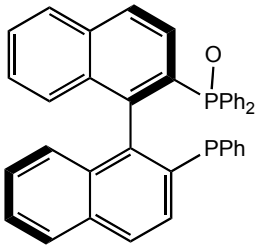
103c (*R*)-Ph-BINEPINE



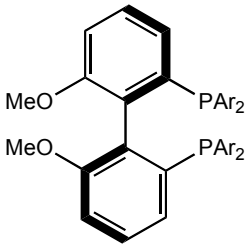
103dR = C_6H_5, R' = C_6H_{11}



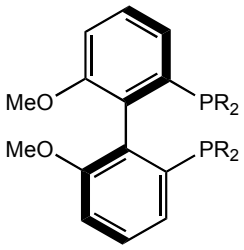
103e (*S*)-MeO-MOP



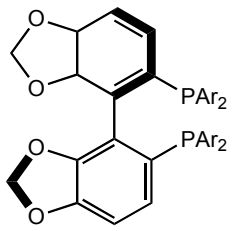
103f (*R*)-BINAPO



103g Ar = 4-Me_2N-C_6H_4, ((*S*)-4-NMe_2)-MeOBIPHEP)
103h Ar = 3,5-*t*-Bu-4MeO-C_6H_2, ((*R*)-(3,5)-MeOBIPHEP)
103i Ar = furyl, ((*R*)-(2-furyl)-MeOBIPHEP)



103j R = *i*Pr, ((*R*)-*i*-Pr-MeOBIPHEP)

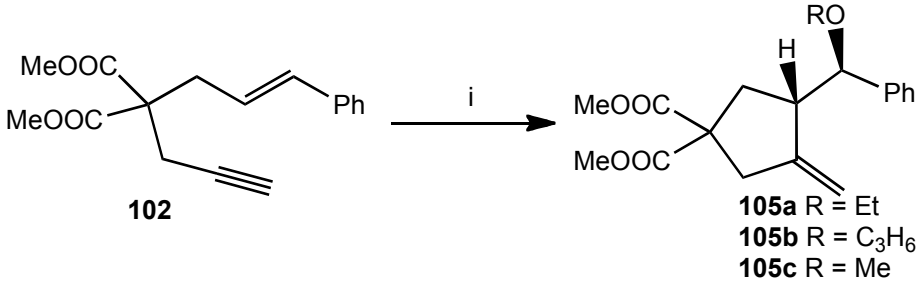


103k Ar = 3,5-*t*-Bu-4-MeO-C_6H_2, ((*R*)-(3,5-*t*-Bu-4-MeO)-SEGPHOS

Figure 8

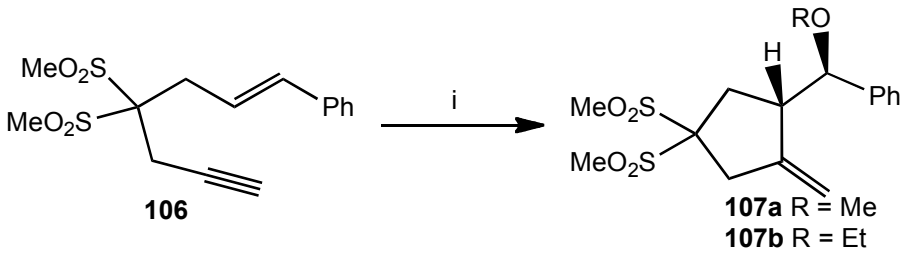
During the investigation compound **103h** appeared as the best atropoisomer ligand (electron rich and sterically hindered). The authors attempted an alkoxycyclisation of compound **102** with the optimised conditions using three different alcohols as solvents: methanol, ethanol and allylic alcohol. The use of ethanol and allylic alcohol gave a better enantiomeric excess of ethers **105a** and **105b** (Scheme 44): 52 and 62% respectively (in comparison of methyl ether **105c** with 30% enantiomeric excess) and good yield (88-89%). When *bis*-sulfonyl-substituted derivative **106** (Scheme 45) was used the catalytic system appeared more efficient (methyl ether **107a** 53% and ethyl ether **107b** 73% enantiomeric excess) caused by the Thorpe-Ingold effect (Scheme 45). The authors decided to study the active gold species formed during the reaction using ^{31}P NMR. As a

study catalytic model the combination of PPh_3, $AuCl_3$ and 3 eq. of $AgSbF_6$. The result showed two peaks assigned as PPh_3AuCl (δ = +33.3 ppm) and $PPh_3(O) \cdot HCl$ (δ = +42.5 ppm). An oxidoreduction process involving PPh_3 as a reducing agent can explain the results. The initial step is conversion PPh_3 to PPh_3Cl_2, which reacts with trace of water giving $PPh_3(O)$ HCl and $AuCl_3$ into AuCl which reacts with another equivalent of PPh_3 giving PPh_3AuCl. The same formation of two products was observed when $AuCl_3$ and (*R*)-MeOBIPHEP were premixed and examined with ^{31}P NMR. The two peaks found correspond to (*R*)-MeOBIPHEP$(AuCl)_2$ (δ = +23 ppm) and related phosphinoxide hydrochloride (δ = +43.3 ppm). Summarised the active gold(I) species, formed during reaction, catalysed the described cycloisomerisation.



Reagents : i) 10 mol% $AuCl_3$, 30 mol% $AgSbF_6$, and 5 mol% **103h**, R.T.

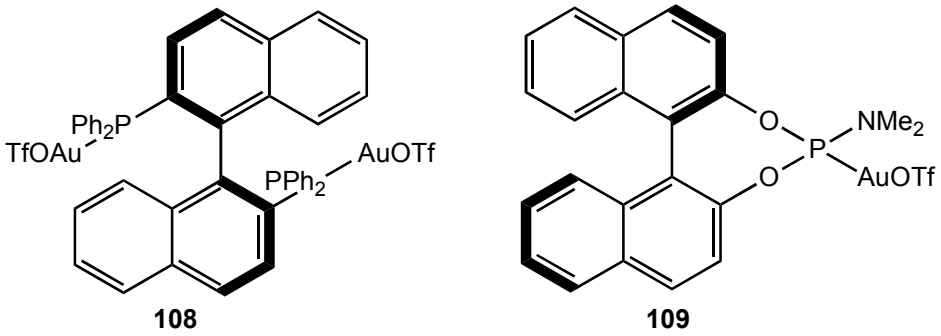
Scheme 44



Reagents : i) 10 mol% $AuCl_3$, 30 mol% $AgSbF_6$, and 5 mol% 46h, 40 ^{o}C.

Scheme 45

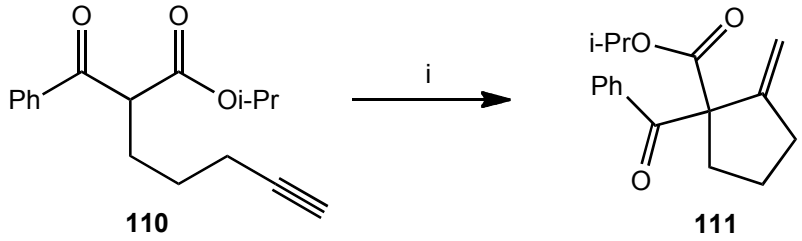
In the literature there are only a few examples of the catalytic enantioselective α-vinylation by addition to alkynes have been described.[74,75] The attempt of Conia-ene reaction using gold(I) complex was attempted by Toste in 2005. Two gold complexes **108** and **109** were investigated (Figure 8).



108 **109**

Figure 8

Treatment of β-ketoester **110** with 5% of cationic gold complexes **108** or **109** in DCM resulted in product **111** in 85 and 80% yield respectively, however no enantioselectivity was observed (Scheme 46).



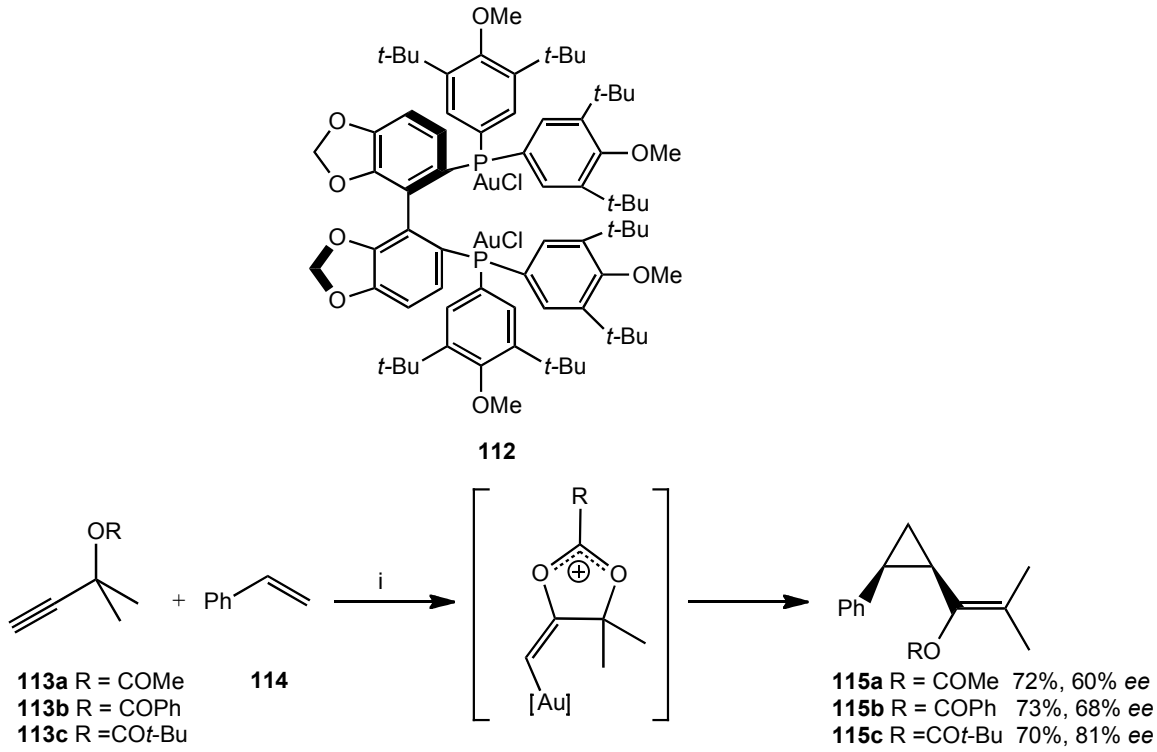
110 **111**

Reagents : i) **108** or **109**, CH_2Cl_2, R.T.

Scheme 46

1.4.2.3a Alkenes Activation - The Enantioselective Intermolecular Cyclopropanation of Olefines – Phosphine Ligand

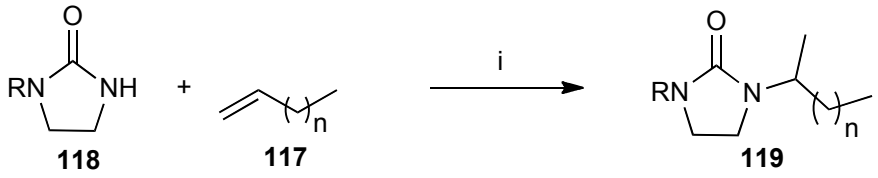
Toste reported in 2005, the enantioselective olefin cyclopropanation catalysed by a gold (I) species tolerates a wide range of monosubstituted, 1,2-substituted, 1,1-substituted, trisubstituted and tetrasubstituted alkenes.[76] During the investigation DTBM-SEGPHOS (**112**) (Scheme 47) was found to be the best chiral ligand for this transformation. Propargyl ester **113a** and styrene **114** were used as the starting materials. The formation of **115a** reached 72% yield with 60% of enantiomeric excess. It was found that the sterically more demanding esters such as pivolate (**113c**) gave a higher enantiomeric excess (**115c**) (Scheme 47). The reaction tolerates halogenated styrenes as well as allyltrimethylsilane. The mechanism of the reaction goes through 1,2-migration to form vinyl-gold carbene species, which converts to *cis*-isomer (Scheme 47).



Scheme 47

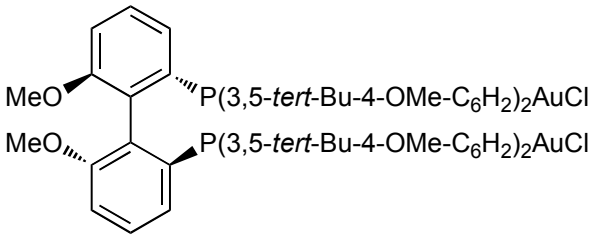
1.4.2.3b Alkenes Activation – The Intermolecular Enantioselective Hydroamination – Phosphine Ligand

In 2009 Widenhoefer reported an intermolecular enatioselective the Markovnikov-selective gold(I) hydroamination reaction of ethylene and 1-alkenes with cyclic ureas.[57] During the optimisation of reaction the best conditions were found and (*S*)-3,5-*t*-Bu-4-MeO-MeOBIPHEP(AuCl)$_2$ (**116**) with achiral AgOTf appeared to be an effective catalytic system for this transformation. The reaction appeared to be general and the scope of 1-alkenes **117** and imidazoline-2-ones **118** was introduced and successfully transferred to hydroamination product **119** with very good yield and high enantioselectivity (Scheme 48, Table 6).



118 **117** **119**

Reagents: i) 2.5 mol% **116**, 5 mol% AgOTf, *m*-xylene, 100 °C.



116

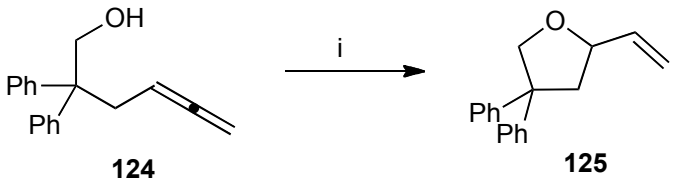
Scheme 48

Table 6

Entry	Nucleophile R =	Alkene n =	Yield [%]	*ee* [%]
1	Me	5	86	76
2	Ph	5	80	71
3	4-C_6H_4F	5	81	74
4	*t*-Bu	5	89	78
5	Me	7	83	73
6	Me	9	76	75

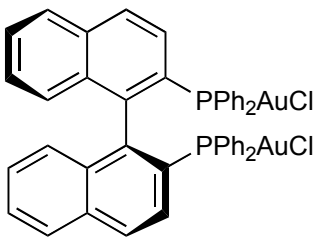
1.4.2.4 Allene Activation – Intramolecular Enantioselective Hydroalkoxylation and Hydroamination of Allenes – Phosphine Ligands

Widenhoefer reported the first enantioselective intramolecular hydroalkoxylation of γ- and δ-hydroxyallenes in 2007 using a gold(I) catalyst.[67] The bidentate phosphine gold chlorides [(BINAP(AuCl)$_2$ (**120**), 3,5-xylyl-BINAP(AuCl)$_2$ (**121**), 3,5-MeO(BIPHEP)(AuCl)$_2$ (**122**), 3,5-MeO(BIPHEP) with 3,5-*tert*-Bu-4-MeO-C_6H_2 as a ligand attached to P (**123**)] were examined with allene **124** to obtain hydroalkoxylation product **125** (Scheme 49).

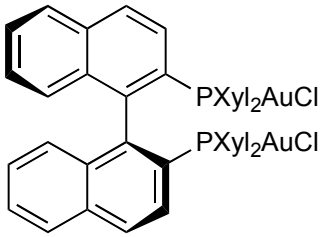


124 **125**

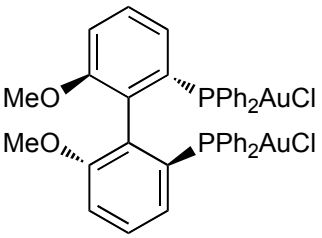
Reagents: 2.5 mol% catalyst, 5 mol% AgX, solvent



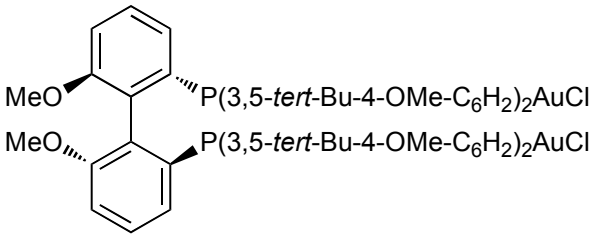
120



121



122



123

Scheme 49

The investigation of 4 different catalysts with dioxane as a solvent and AgOTf as a co-catalyst showed that the best enantiomeric excess (86% *ee* in 75% yield) can be obtained with electron rich and sterically hindered **123** catalyst. The reaction is highly depended on silver co-catalyst and AgOTf is the most significant in a range of different silver salts (Table 7).

Table 7

Entry	Silver salt	Yield [%]	*ee* [%]
1	$AgAsF_6$	36	26
2	$AgSbF_6$	47	31
3	$AgClO_4$	28	38
4	AgOAc	0	-
5	AgOTf	75	86

The non-polar solvents (toluene and dioxane) gave higher enantioselectivity then polar solvents (tertahydrofuran, ethyl acetate, acetone, acetonitrile and methanol) (Table 8). The slightly better enantiomeric excess (94%), using toluene, was reached, when temperature was decreased to -20 °C however the time of the reaction increased to 61 h to get the same yield.

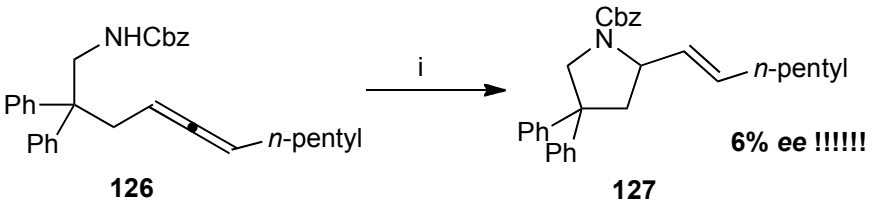
Table 8

Entry	Solvent	Time [h]	Yield [%]	*ee* [%]
1	dioxane	2	75	86
2	toluene	4	73	90
3	THF	4	75	83
4	ethylacetate	2	75	81
5	acetone	1	93	41
6	acetonitrile	2	90	44
7	methanol	47	91	22

The reaction appeared to be general and many 2-vinyltetrahydrofurans were synthesised. The γ-hydroxyallenes β-substituted as well as δ-hydroxyallenes β-substituted with axially chiral allene gave enantiomerically and isomerically pure product. When a racemic allene was introduced into the reaction, different ratios of isomers (*cis* and *trans*) were obtained, however each of them with high enantiomeric excess. However, when racemic allenyl alcohol with unsubstituted β-position was introduced to reaction, the

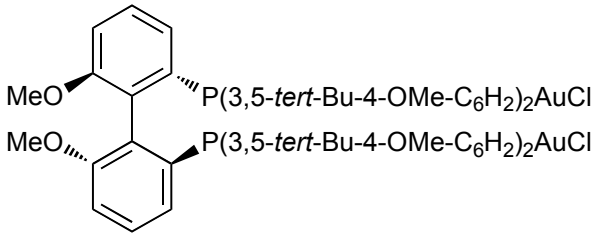
stereoisomer obtained despite high yield showed poor enantioselectivity. The mechanism of hydroalkoxylation starts from the complexation of gold to the internal allenyl C=C bond forming a gold-allene complex, followed by the cyclisation of gold-allene complex with deprotonation/protonolysis.

In the same year, Widenhoefer reported another enantioselective transformation - intramolecular enantioselective hydroamination reaction of *N*-(γ-allenyl) carbamates.[77] Using [(*S*)-3,5-*t*-Bu-4-MeO-MeOBIPHEP]Au_2Cl_2 (**123**) with $AgClO_4$, 1,3-disubstituted allenyl compound **126** was successfully transformed to pyrrolidine **127** with high diastereoselectivity and good yield but low enantiomeric excess (Scheme 50).



126 **127**

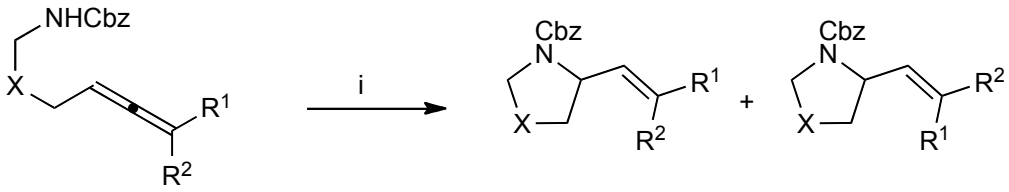
Reagents: 2.5 mol% **123**, 5 mol% $AgClO_4$, *m*-xylene, -20 °C, 86% yield, *E:Z* 25:1.



123

Scheme 50

When chiral trisubstituted allenes **128** were introduced to the reaction, the diastereoselecivity appeared to be decreased but enantioselectivity increased (Scheme 51, Table 9). The reaction showed strong influence between enantioselectivity and substituted allenyl chain as well as substituted β-position.



128 (*Z*)-**129** (*E*)-**129**

Reagents: 2.5 mol% **123**, 5 mol% $AgClO_4$, *m*-xylene, 23 °C.

Scheme 51

Table 9

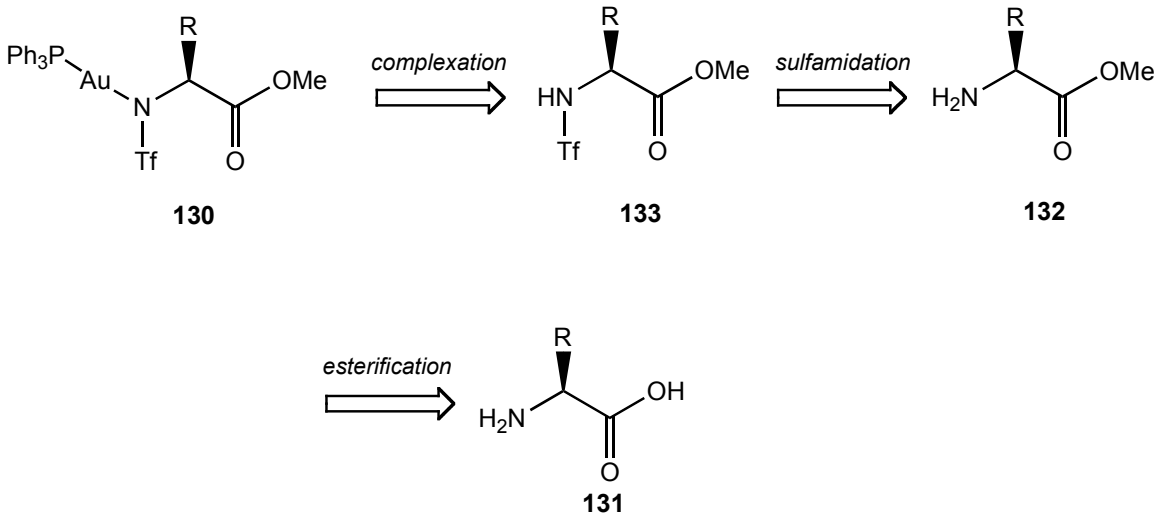
Entry	X	R^1	R^2	Yield (*Z*)-**129**+ (*E*)-**129** [%]	(*Z*)-**129** : (*E*)-**129**	*ee* (*Z*)-**129**(%)	*ee* (*E*)-**129**(%)
1	CPh_2	Me	Et	94	3.1:1	96	76
2	CPh_2	Me	*n*-hexyl	99	10.1:1	91	9
3	CPh_2	Me	*i*-Bu	99	2.6:1	97	54
4	CPh_2	Me	*t*-Bu	52	1:25	2	-
5	CPh_2	Et	*n*-hexyl	86	4.3:1	84	47
6	CH_2	Me	*n*-hexyl	87	2.4:1	75	45

2. Results and Discussion

It has been recently shown based on the work of Gagosz[44,78,79] and Michelet,[46] that gold complexes can both have catalytic activity and be air stable. This thesis is a modification of the air stable catalyst $Ph_3PAuNTf_2$ to give a new chiral agent, which could be investigated as a potential new chiral catalyst.

2.1 First Generation Gold(I) Complexes (Chirality on X Ligand)

We decided to exchange one of the triflate groups with a chiral compound. Regarding the cost, variety of compounds and availability we utilised amino acids as a source of chirality. Scheme 52 shows the synthetic approach.



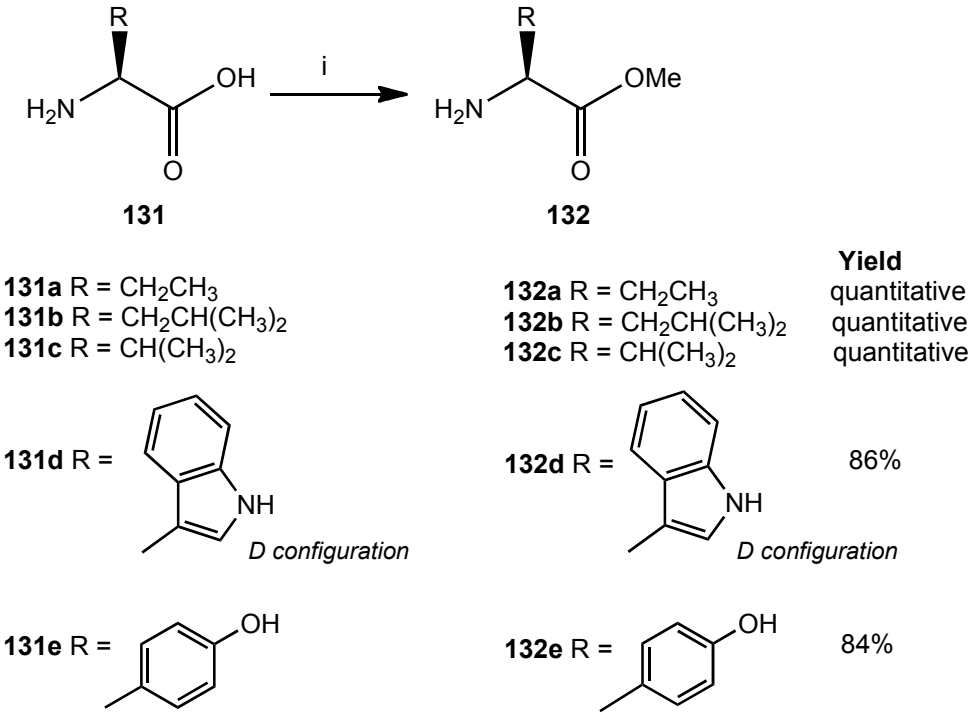
Scheme 52

2.1.1 Synthesis of Esters

The esterification reaction is very well known, and was first described by Fisher in 1895 and named after its inventor 'Fisher esterification'.[80] This classic esterification involves the acid catalysed (i.e. sulfuric acid) reaction of an organic acid and alcohol in the presence of a dehydrating agent because of the hydrolysis equilibrium constant which means that the reaction is highly reversible.[81] This disadvantage can be also solved using the alcohol as the solvent in reaction, or to remove water as azeotrope. Since 1895 many methods have been invented to prepare esters from carboxylic acids.[82,83] The esterification of carboxylic acids with alcohols can be realised using Steglich method[84] with

dicyclohexylcarbodimide (DCC) and 4-dimethylaminopyridine (4-DMAP) as a catalyst or alcoholysis of acyl chlorides prepared *in situ*.[85]

The alcoholysis of acyl chlorides was chosen due to the irreversibility of the reaction, ease of maintaining anhydrous conditions and simple work-up.[85] The simple esterification reaction of amino acid **131**, carried out in methanol in presence of $SOCl_2$ giving appropriate aminoester **132** (Scheme 53). The yield quantitative was obtained with compound **131a**, **131b**, **131c**. With compounds **131d** and **131e**, the yield reached 86% and 84% respectively.



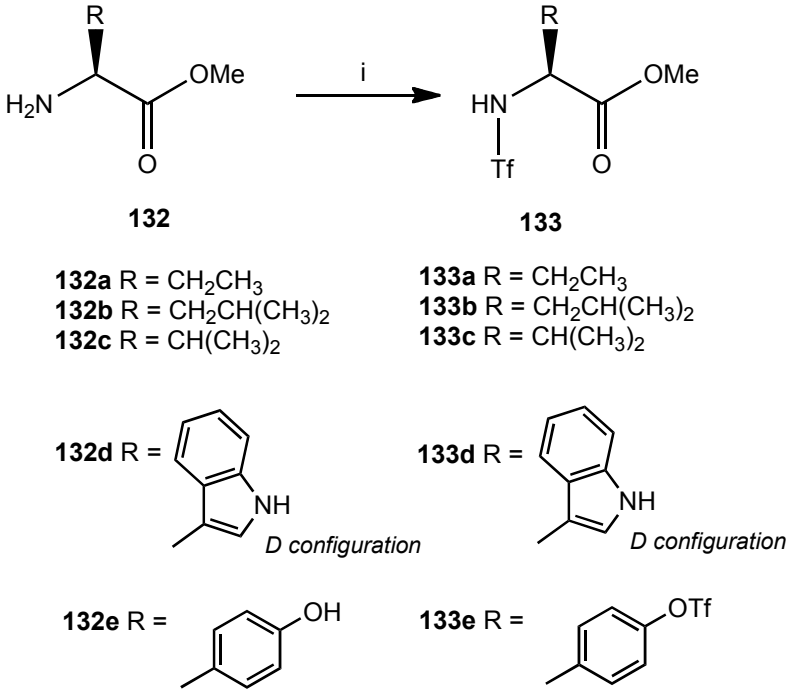
Scheme 53

2.1.2 Synthesis of Tryflic Amines (Sulfonamides)

Sulfonamides can be prepared by treating sulfonyl chloride or anhydride with amine in the presence of base.[86] The sulfamidation reaction can lead to sulfonamides and sometimes unwanted bis-sulfonamides, which can be converted to mono-sulfonamides in a base-induced hydrolysis. The formation of bis-sulfonamides depends on the reactivity of

the sulfonamides; this depends on the nature of the group attached to the nitrogen of the amine and substituent in sulfonyl chloride or anhydride.[86]

The classic method of preparing sulfamides, using an amine and an anhydride, was used in next step of synthesis; aminoester **132a** was used as a model substrate. The triflic imide **133a** was synthesised in good yield according to the procedure used by Duncia,[85] using trifluoromethanesulfonic anhydride in the presence of triethylamine (Scheme 54). The same experimental conditions were used with compounds **132b**, **132c**, **132d**, **132e** (Table 10). However triflation of the phenol in compound **132e** occurred (Figure 9).



Reagents : i) Tf_2O, CH_2Cl_2.

Scheme 54

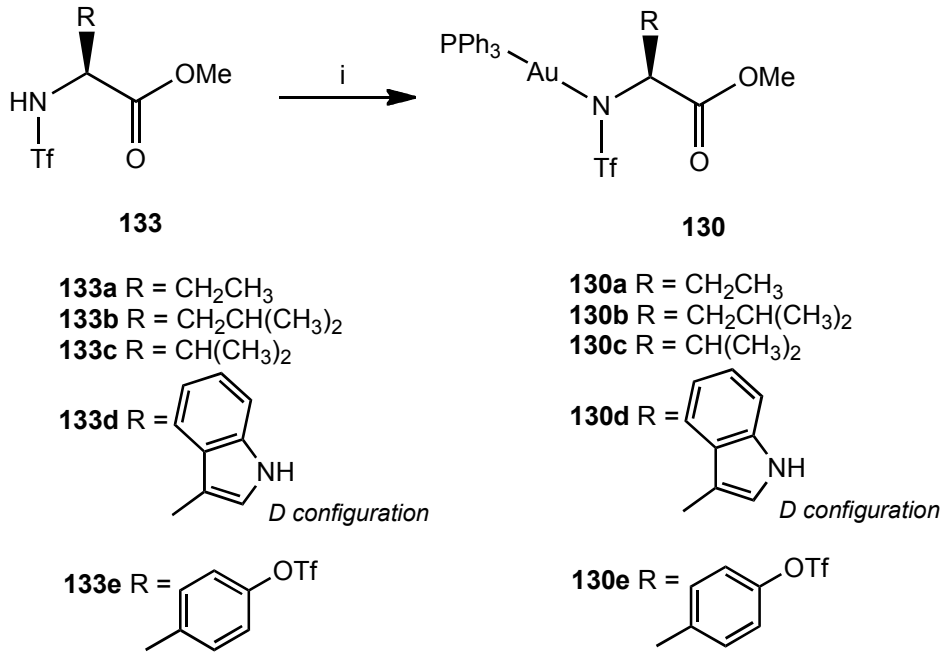
Table 10

Entry	Substrate	Product	Yield [%]
1	**132a**	**133a**	85
2	**132b**	**133b**	77
3	**132c**	**133c**	72
4	**132d**	**133d**	90
5	**132e**	**133e**	49

Figure 9

2.1.3 Synthesis of Gold(I) Complex

The Au(I) complexes **130a**, **130b**, **130c**, **130d**, **130e** were synthesised from Ph_3PAuCl, Ag_2CO_3 and the corresponding chiral ligand, following the methodology described by Gagosz with good to excellent yields (Scheme 55) (Table 11).[44]



Reagents : i) Ph_3PAuCl, Ag_2CO_3, CH_2Cl_2, RT.

Scheme 55

Table 11

Entry	Substrate	Product	Yield [%]
1	**133a**	**130a**	quantitative
2	**133b**	**130b**	97
3	**133c**	**130c**	91
4	**133d**	**130d**	93
5	**133e**	**130e**	quantitative

Finally, five new gold compounds were synthesised. They were found to be as storable and air-stable as gold catalyst **30** (Gagosz catalyst). The gold complexes were successfully crystallised. The crystal structures are shown in Figure 10 for **130a**, Figure 11 for **130b**, Figure 12 for **130c**, Figure 13 for **130d**, Figure 14 for **130e**. The crystal structure of gold compound **130a** shows rotation between C25 and C28 which shows two conformers are possible with different length of the bonds [Å]: Au(1)-N(1) 2.068(4), Au(2)-N(2) 2.044(4) and Au(1)-P(1) 2.2307(12), Au(2)-P(2) 2.2307(12). The gold compound **130c** showed only one conformer with the length of the bonds [Å]: Au-N 2.079(3) and Au-P 2.2292(10). These results suggest that isopropyl group prevents rotation due to steric hindrance.

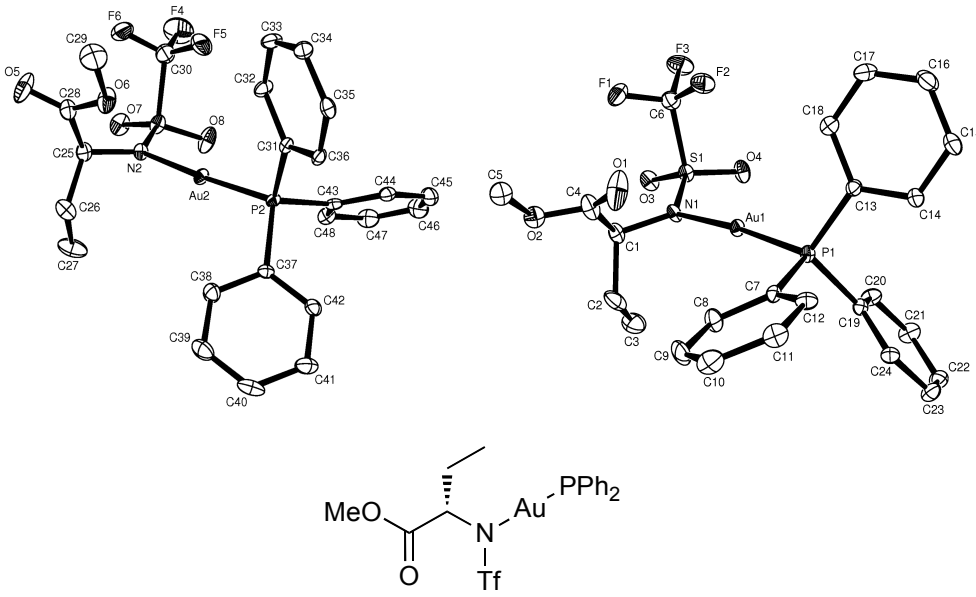
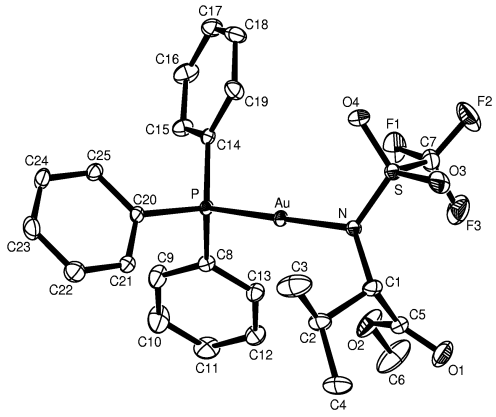


Figure 10



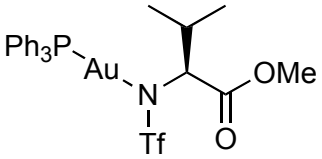
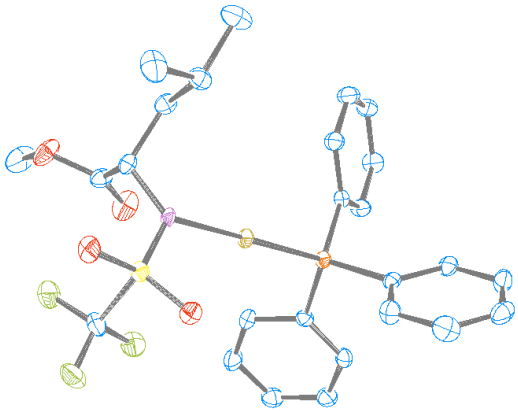


Figure 11



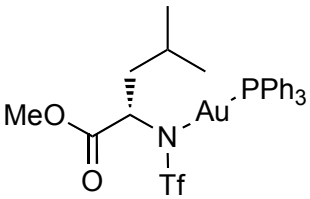
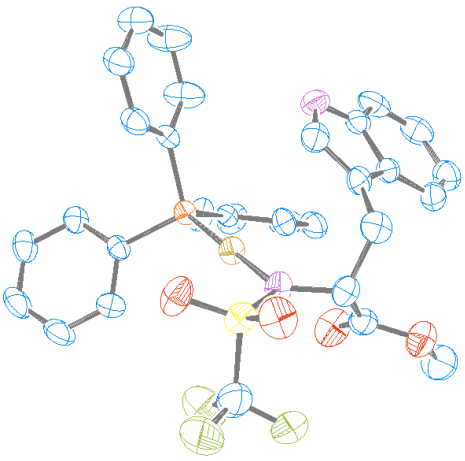


Figure 12



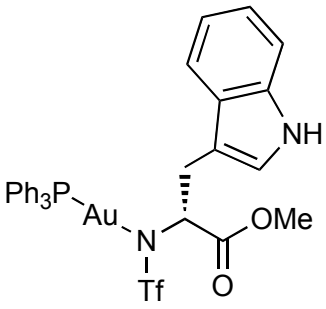


Figure 13

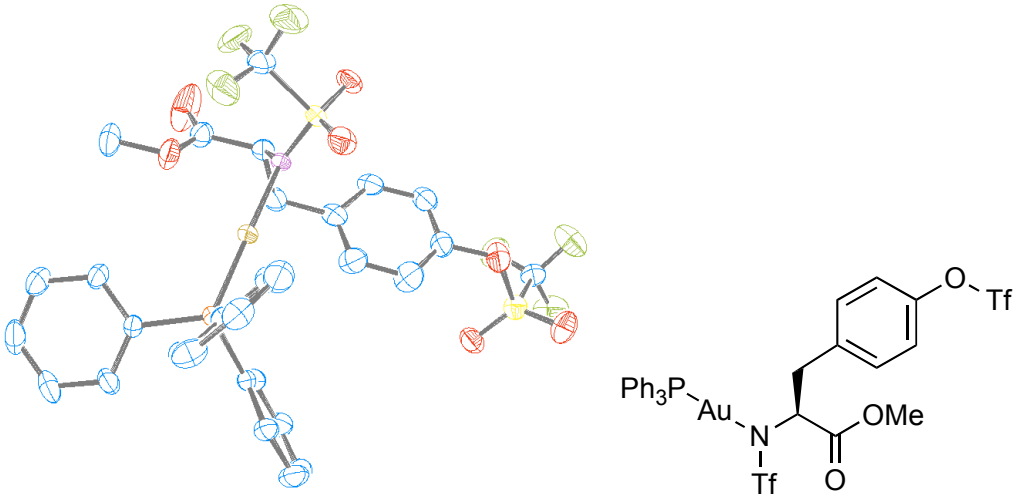
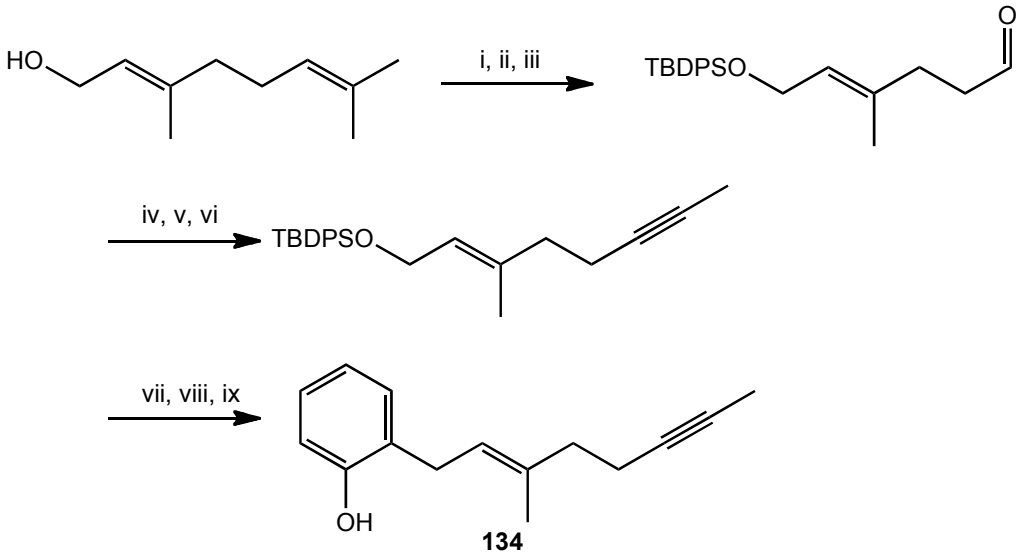


Figure 14

2.1.3 Synthesis of The Model Substrate for Cycloisomerisation

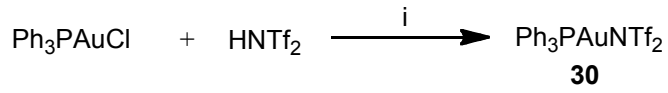
A model substrate enyne **134** was chosen as a suitable compound to be investigated with the newly synthesised gold(I) complex. Substrate **134** has been previously reported by Michelet in the gold(I) catalysed cycloisomerisation,[46] The synthesis of 1,5-enyne **134** is shown in Scheme 56.[46,87]



Reagends: i) TBDPSCl, imidazole, Et_3N, DMF, 0 °C; ii) MCPBA, $CHCl_3$, 0 °C; iii) HIO_4 H_2O, THF, 0 °C; iv) Zn, Ph_3P, CBr_4, CH_2Cl_2, 0 °C; v) *n*-BuLi, Et_2O, 0 °C; vi) *n*-BuLi, CH_3I, THF, 0 °C; vii) TBAF, THF, RT; viii) PBr_3, Et_2O, 0 °C; ix) phenol, NaH, toluene, RT.

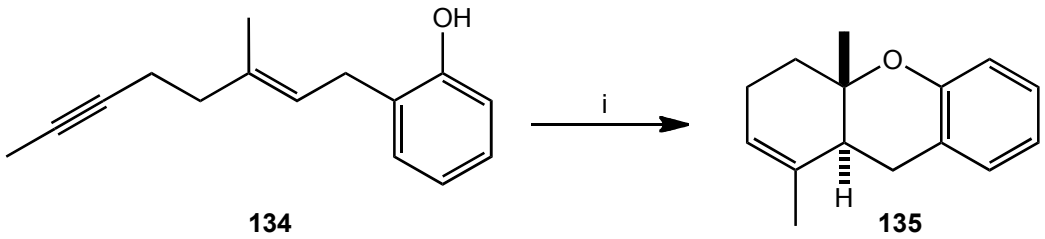
Scheme 56

A sample of the expected tricycle **135**, was obtained by cyclisation of enyne phenol **134** following Michelet's procedure (Scheme 58).[46] The catalyst $Ph_3PAuNTf_2$ (**30**) was prepared following Gagosz's procedure: through mixing triphenylphosphine gold chloride with trifluoromethanesulfonamide in the presence of silver carbonate (Scheme 57).[44] Triphenylphosphine gold chloride is commercially available, however preparation of it is relatively easy using Lewis' procedure involving tetrachloroauric acid trihydrate and triphenylphosphine in acetone in 82% yield.[88] The tetrachloroauric acid trihydrate, as triphenylphosphine gold chloride, is commercially available. It can also be synthesised using Troshin procedure by dissolving gold metal in *aqua regia* (nitric acid:hydrochloric acid, in a volume ratio 1:3) followed by repeated evaporation with conc. hydrochloric acid then water.[89] The Gagosz catalyst (**30**) was synthesised using described methods (Scheme 57), however in our case, 2 mol% of **30** was needed to effect the cyclisation (after 1.5 h with 1 mol% of the catalyst still a lot of starting material in reaction), whereas the author described using only 1 mol%.[46] The tricycle **135** was obtained in 86% yield (Michelet, 76%) (Scheme 58).



Reagents : i) Ag_2CO_3, CH_2Cl_2, RT.

Scheme 57



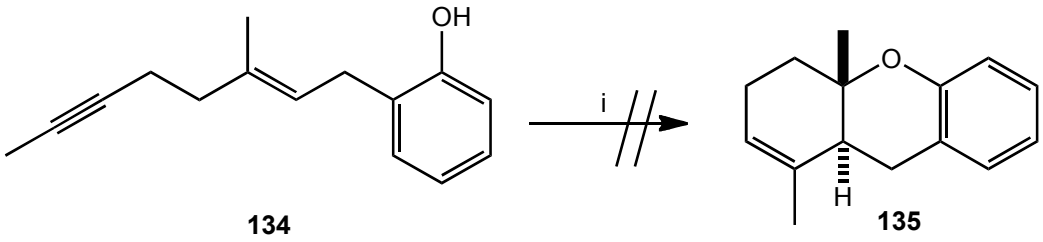
Reagents : i) **30**, Et_2O, RT, 86%.

Scheme 58

2.1.4 First Generation Gold(I) Complex as a Catalyst for Cycloisomerisations (Chirality on X Ligand)

2.1.4.1 Solvent Investigation

As Michelet reported, the reaction can be prepared in a variety of solvents including diethyl ether, toluene or dichloromethane.[46] These three solvents were investigated with the new chiral gold(I) compound **130a** (Scheme 59), however cycloisomerisation did not occur in any of these solvents. A number of solvents, starting from non-polar (toluene, dioxane, diethyl ether) through polar aprotic (dichloromethane, DCE, THF, acetone, DMF, MeCN) to polar protic (methanol) previously used with success in different gold catalysed transformations, were investigated.[2] The increase of temperature did not lead to the expected cycloisomerisation product and even the addition of catalytic amount of base to encourage cyclisation did not work (Table 12).



134 **135**

Reagents : i) **130a**, Et_2O, RT.

Scheme 59

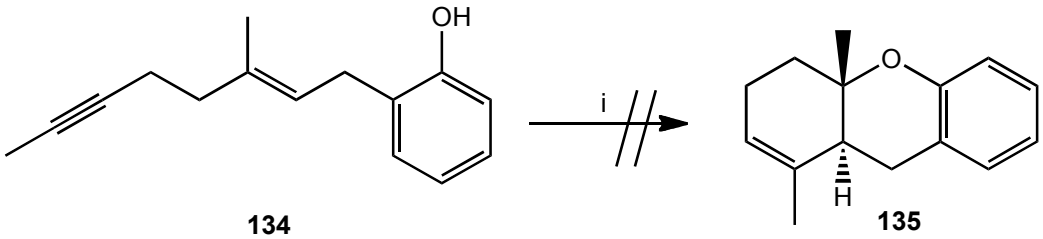
Table 12

Entry	Solvent	Amount of **130a** [mol%]	Additive	Temp. [°C]	Results
1	Et_2O	5	-	RT[c]	/[b]
2	Et_2O	25	-	RT[c]	/[b]
3	Et_2O	5	NaH (after **130a**)	RT[c]	/[b]
4	Et_2O	5	NaH (before **130a**)	RT[c]	/[b]
5	Et_2O	5	CH_3OK(after **130a**)	RT[c]	/[b]
6	Et_2O	5	Drop of H_2O	RT[c]	/[b]
7	Et_2O	5	Drop of HCl	RT[c]	/[b]
8	Toluene	5	-	RT to 40[c]	/[b]
9	Toluene	5	-	65[c]	/[b]

10	Toluene	5	-	reflux[c]	/[b]
11	CH_2Cl_2	5	-	reflux[a]	/[b]
12	DCE	5	-	reflux[a]	/[b]
13	$CHCl_3$	5	-	reflux[a]	/[b]
14	Dioxane	5	-	reflux[a]	/[b]
15	THF	5	-	reflux[a]	/[b]
16	DMF	5	-	reflux[a]	/[b]
17	CH_3CN	5	-	reflux[a]	/[b]
18	CH_3OH	5	-	reflux[a]	/[b]
19	Acetone	5	-	reflux[a]	/[b]
20	---	5	-	65	/[b]

(a) Reaction was stirred for 2-3 h at RT, controlled by TLC and refluxed for 24 h; (b) Starting material was recovered; (c) Reaction was stirred for 24 h.

The same negative results were obtained when gold compounds **130b**, **130c**, **130d** and **130e** (Scheme 60) were used as catalysts with enyne **134** (Scheme 60). Diethyl ether, toluene and dichloromethane were investigated as solvents (Table 13), which were suggested and successfully used by Michelet on phenol **134**.[46]



134 **135**

Reagents : i) **130b** or **130c** or **130d** or **130e**, solvent.

Scheme 60

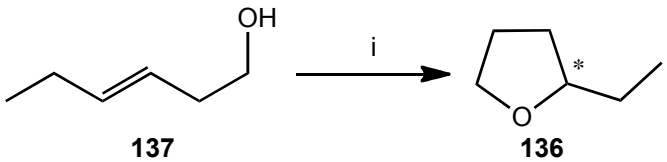
Table 13

Entry	Au-complex	Amount of Au-compound [mol%]	Solvent	Temp. [°C]	Results
1	**130b**	5	Et_2O	RT	/[b]
2	**130c**	5	Et_2O	RT	/[b]
3	**130d**	5	Et_2O	RT	/[b]
4	**130e**	5	Et_2O	RT	/[b]
5	**130b**	5	Toluene	reflux[a]	/[b]
6	**130c**	5	Toluene	reflux[a]	/[b]
7	**130d**	5	Toluene	reflux[a]	/[b]
8	**130e**	5	Toluene	reflux[a]	/[b]
9	**130b**	5	CH_2Cl_2	reflux[a]	/[b]
10	**130d**	5	CH_2Cl_2	reflux[a]	/[b]

(a) Reaction was stirred for 2-3h at RT, controlled by TLC and refluxed for 24 h; (b) Starting material was recovered.

2.1.5 Attempt Synthesis of Chiral Furan Using First Generation Gold(I) Complex

The new synthetic method for chiral tetrahydrofurans (**136**) using gold-compounds throughout activation of C-C double bonds for the addition of O-nucleophiles was investigated. The gold compound **130a** was used in reactions as a chiral gold catalyst. *Trans*-3-hexen-1-ol **137** was used as the starting material (Scheme 61, Table 14) to avoid side reactions. The 5-*endo*-trig cyclisation is disfavoured according to Baldwin's rules.[90,91] Diethyl ether, toluene and THF were used as solvents and the reactions were carried out at ambient temperature. The product **136** was not obtained despite the use of a catalytic amount of base (Entry 2 and 4, Table 14).



137 **136**

Reagents : i) **130a**, solvent.

Scheme 61

Table14

Entry	Amount of **130a** [mol%]	Solvent	Additive [Eq.]	Results
1	25	Et_2O		/[b]
2	25	Et_2O	NaH [0.1]	/[b]
3	25	Toluene		/[b]
4	25	THF	NaH [0.1][a]	/[b]

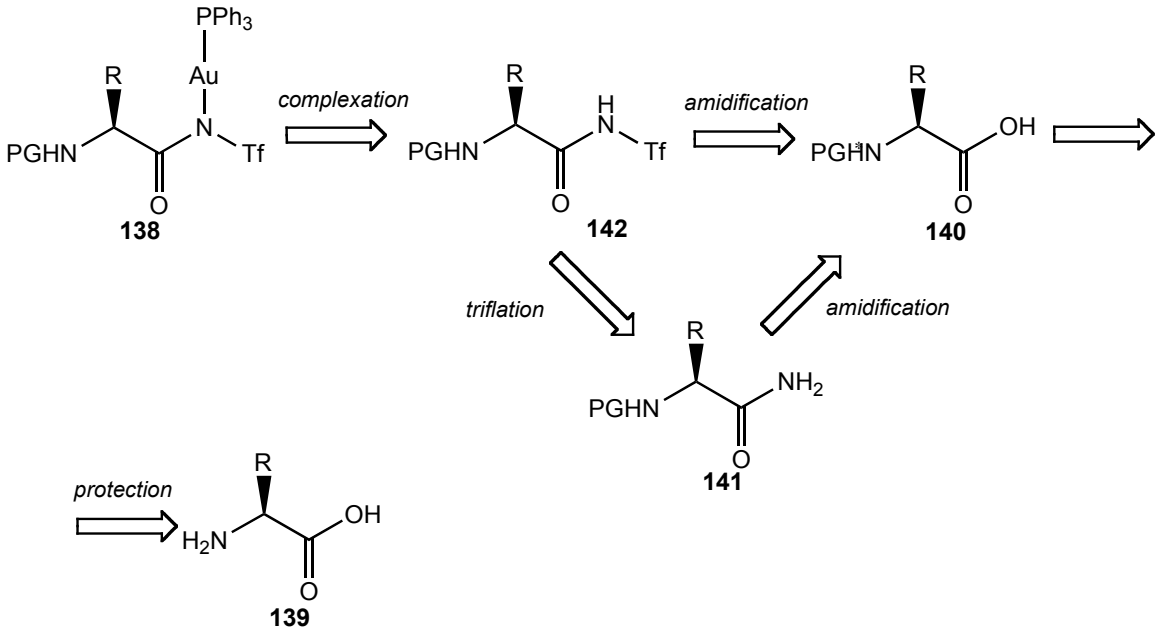
(a) Added after 24h of stirring; (b) Starting material was recovered.

2.1.7 Comparison of ^{31}P Shift with Catalytic Activity

During this investigation, five new stable gold compounds were synthesised. The ^{31}P NMR chemical shift of compounds **130a**, **130b** and **130c** is 31.57 ppm, which is around 1 ppm bigger then highly active compound **30** (30.6 ppm - Gagosz catalyst), and compounds did not show catalytic activity. The compounds **130e (**base on (*L*)-thyrosin) and **130d** (base on (*D*)-tryptophan) gave smaller ^{31}P NMR chemical shifts 31.30 ppm and 31.01 ppm respectively, closer to 30.6 ppm (**30** – Gagosz catalyst), however no catalytic activity was observed. The rationalisation of these results will be described in Chapter 2.3.

2.2 Second Generation Gold(I) Complex (Chirality on X Ligand)

It was decided to modify the gold chiral compounds to increase the positive charge on gold (decrease the stability of the ligand and of the same time increase reactivity), which may shift the phosphorous signal to the range of 30.6 ppm (corresponding PPh_3 in **30** Gagosz catalyst). This can be considered as 'an indicator' of reactivity or more likely to be as ionic character of the bond between gold and 'counterion'. The chiral amide with attached gold species and triflic group was set as a target (**138**). The synthetic approach is presented in Scheme 62.



Scheme 62

The first step is a protection of the amine **139** (i.e. Boc, Cbz, reductive amination) to obtain *N*-protected aminoacid **140**. Using a condensation reaction to form the amide, compound **142** could be prepared directly with triflic amide or in two steps: amide formation with ammonia (**141**) followed by triflation with triflic anhydride. The final step is complexation of the triphelylphosphine gold chloride with amide **142**.

2.2.1 Protection of Amine Group on (*L*)-leucine

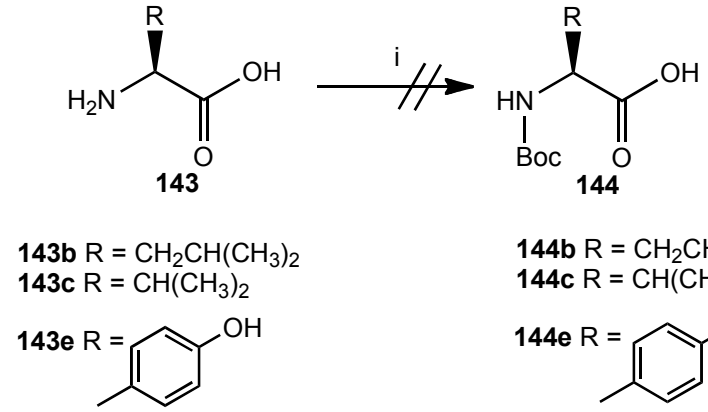
The protection of the amine is an essential step in peptide chemistry.[92] The three different clauses protecting groups can be categorised by their method of removal:

a) Protecting groups removed by acid (i.e. Boc, Trt, Ddz, Bpoc, Nps)

b) Protecting groups removed by base (i.e. Fmoc, Nsc, Bsmoc, TCP, Esc)

c) Other protecting groups (i.e. Cbz, Alloc, *o*NBS, Bts, Bn)

Initially, the Boc group was used as a protective group as it is stable towards most nucleophiles and bases. Three amino acids **143b**, **143c**, **143e** were used for a protection (Scheme 63) using four different protocols without success.[93-95] The conditions and results are shown in Table 15.



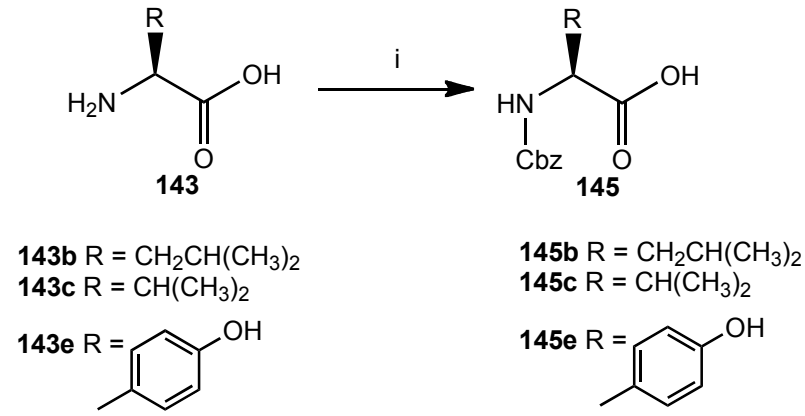
Reagents : i) $(Boc)_2O$, solvent, base.

Scheme 63

Table 15

Entry	Starting material	Solvent	Base [Eq.] or [solution %]	Product	Yield [%]
1	**143b**	THF	Et_3N [3]	**144b**	0
2	**143c**	H_2O/THF	$NaHCO_3$ [3]	**144c**	0
3	**143c**	CH_3OH	Et_3N [10%]	**144c**	0
4	**143e**	THF	Et_3N [3]	**144e**	0
5	**143e**	H_2O/THF	$NaHCO_3$ [3]	**144e**	0
6	**143e**	DMF	Et_3N [10%]	**144e**	0

Next benzyl chloroformate (Cbz) was used as a protecting group and is highly stable to base and mild acidic condition.[92] The protection of compounds **143b**, **143c** and **143e** were attempted using known procedures (Scheme 64).[96-98] The conditions and results are shown in Table 16. For the next transformation the Cbz-(*L*)-leucine **145b** was used due to more steric group placed in α position (isobutyl group).



Reagents : i) CbzCl, solvent, additive.

Scheme 64

Table 16

Entry	Starting material	Solvent	Additive	Product	Yield [%]
1	**143b**	2M NaOH aq.	---	**145b**	76
2	**143c**	2M NaOH aq.	Et_2O	**145c**	92
3	**143e**	1M NaOH aq.	---	**145e**	0

2.2.2 Synthesis of Triflic Amide ((*L*)-leucine)

The amide bond formation is the most important reaction in peptide synthesis, however the realisation of the reaction through simple mixing of an acid with an amine results in an acid-base reaction with the formation of a stable salt.[99] A solution for this problem is the activation of the acid to nucleophilic attack by the amine. This can be achieved by the addition of a leaving group. Many methods of amide formation by activation of carboxylic acids have been developed[100] including: acyl halides, acyl azides, acylimidazoles using CDI, anhydrides and alkyl esters.

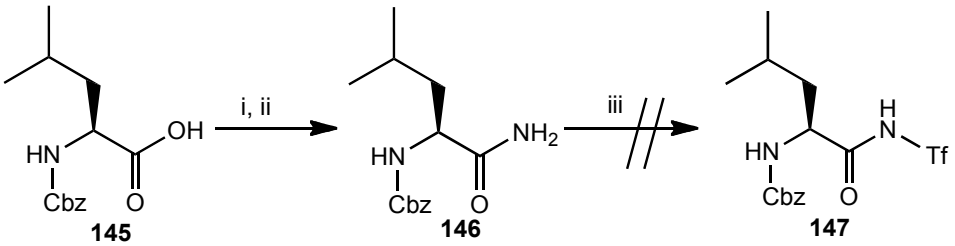
To prepare amide **142** (Scheme 62) there were two different retrosynthetic analyses, presented in section 2.2:

a) Formation of amide followed by the triflation of amide nitrogen

b) Direct formation of triflic amide using trifluoromethanesulfonamide

For triflic amide synthesis, compound **145** (Scheme 65) was used. The mixed carbonic anhydride method was chosen. The method relies on the difference in reactivity

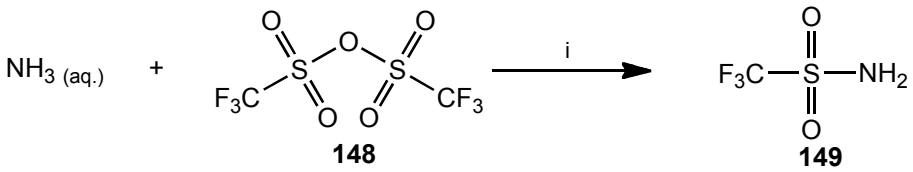
of the carbonyl groups. The carbonate electrophilic centre is more reactive then carboxylic side of carbonic anhydride due to less stabilisation by resonance. Following Eldo's procedure,[94] the compound **146** was synthesised successfully (82%). However the triflation of a amide nitrogen using a modified procedure of Bergeron to obtained **147**, was not successful (Scheme 65).[101]



Reagents : i) CH_3COCl, Et_3N, DCM/Dioxane, -5 °C; ii) $NH_{3\ (aq.)}$, RT; iii) $(CF_3SO_2)_2O$, *t*-BuLi, THF, -78 °C.

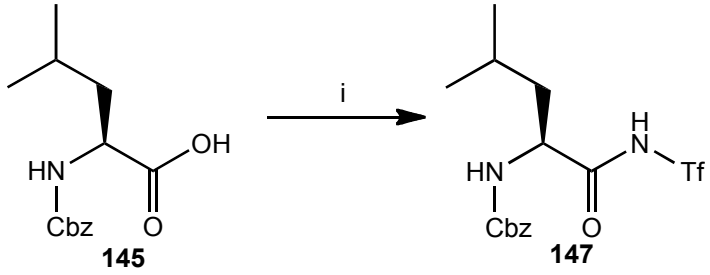
Scheme 65

The direct amide formation was achieved using the trifluoromethanesulfonamide **149** which was prepared in 89% yield from triflic anhydride **148** and a 37% solution of ammonia in water at 0 °C for 12 h following Burdon's procedure (Scheme 66).[102]



Scheme 66

Direct amide formation of acid **145** with triflic amide **149** in presence of EDC and HOBt·H_2O in dichloromethane gave amid compound **147** in 53% yield (which improved to 64% when the reaction was scaled up) (Scheme 67).[96] The advantage of using EDC is that the resulting urea is water-soluble and can be easily removed after the reaction. The mechanism goes through an *O*-acylisourea as a product of the reaction of the acid and the carbodiimide (in our case EDC). The *O*-acylisourea can directly react with an amine to give the desired amide and urea as a side product (formation of urea is a driving force of the reaction). However the side reaction of racemisation and acetyl transfer (which forms *N*-acylurea) can result in lower yields. This problem can be avoided using a selected nucleophile (in this case HOBt), which reacts faster than competing side reactions. The resultant intermediate reacts with the amine to yield the desired amide.

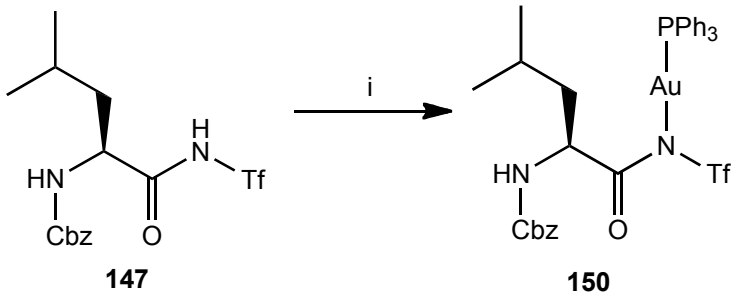


Reagents : i) $CF_3SO_2NH_2$, HOBt*H_2O, EDC, CH_2Cl_2, 64%.

Scheme 67

2.2.3 Synthesis of Gold(I) Complex Based on (*L*)-leucine

Compound **147** has two acidic protons: the proton attached to the protected amine group and the proton attached to amide part of the compound. Both can be abstracted in basic conditions. The amide part (Scheme 68) possesses a structure similar to the imine. This means the proton attached to the amide nitrogen is very acidic and the triflic group, which is one of the most powerful electron-withdrawing groups, increasing the acidity even further. The first addition of Ph_3PAuCl in the presence of Ag_2CO_3 (affinity of silver for chlorides and weak conjugated base) in DCM (C=0.04 M) at room temperature using Gagosz's procedure gave only a mixture of compounds and residual Ph_3PAuCl (33.2 ppm, ^{31}P NMR) (Entry 1, Table 17). When the reaction was carried out in dry THF with NaH, a mixture of two compounds were obtained with 33.2 ppm (corresponding to Ph_3PAuCl) and 32.2 ppm shift (^{31}P NMR) (Entry 4, Table 17). The mixture was used in a cyclisation reaction with enyne phenol **134** in dichloromethane, however no product was observed. A few different approaches were used to obtain desired compound **150** from **147**, but only a mixture of compounds and starting material were observed (Table 17).



Reagents : i) additives, solvents, temperature - see Table below.

Scheme 68

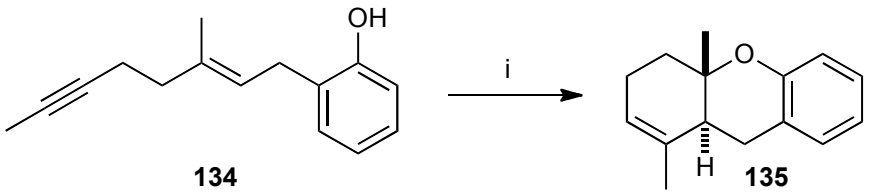
Table 17

Entry	T [°C]	Solvent	Additive (eq.)	Concentration [M]	Product ^{31}P NMR ppm/%
1	RT	DCM	Ag_2CO_3 (1)	0.04	33.2
2	RT	THF	Ag_2CO_3 (1), NaH (1.1), TMSCl (1.3)	0.1	33.2
3	RT	DCM	Ag_2CO_3 (1), NaH (1.1)	0.1	32.2, 31.0
4	RT	THF	Ag_2CO_3 (1), NaH (1.1)	0.1	33.2, 32.1
5	RT	DCM	NaH (1.1)	0.1	33.2, 32.2
6	RT	DCM	Ag_2CO_3 (1)	0.1	31.1(30), 30.6(70)
7	0 to 10	DCM	Ag_2CO_3 (1.8)	0.1	31.1(26), 30.6(74)

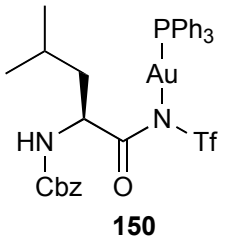
Entry 6 and 7 using only Ag_2CO_3 and concentration 0.1M gave the desired product with a chemical shift of 30.6 ppm (^{31}P NMR), which corresponds to the chemical shift of the Gagosz catalyst **30** (30.6 ppm). This result suggests that the obtained product could have catalytic properties (the rationalisation is described in Chapter 2.3). In both entries the product obtained was not pure, however the ratio in Entry 7 is slightly better. In both cases the reaction is slow and not finished after 5 h (33.2 ppm : 30.6 ppm, 59% : 41%). The crystallisation of the gold(I) complex was attempted using a slow diffusion method with variety of solvents and temperatures, however crystals were not obtained.

2.2.3.1 Second Generation Gold(I) Complex Based on (L)-leucine as a Catalysts in Cycloisomerisation

The next step was to use the mixture from Entry 7, Table 12 in cycloisomerisation reaction. Without purification, ^{31}P NMR was used to calculate that 74% of the phosphorous atoms, with a chemical shift of 30.6 ppm, are assigned to our active compound. The reactions proceeded under nitrogen with 0.5 M concentration. The mixture was used successfully in the cyclisation reaction (Scheme 69) of tricycles compound **135** (Table 18).



Reagents: i) **150**, CH_2Cl_2 or C_6H_6, RT.



Scheme 69

Table 18

Entry	Mol% of **150**	Solvent	Time	$[\alpha]_D$	Yield of **135** [%]
1	27	DCM	16 h	0	76
2	5	DCM	5 Days	0	70
3	5	DCM[a]	5 Days	0	78
4	5	Benzene	5 Days	0	63

(a) Laboratory reagent grade.

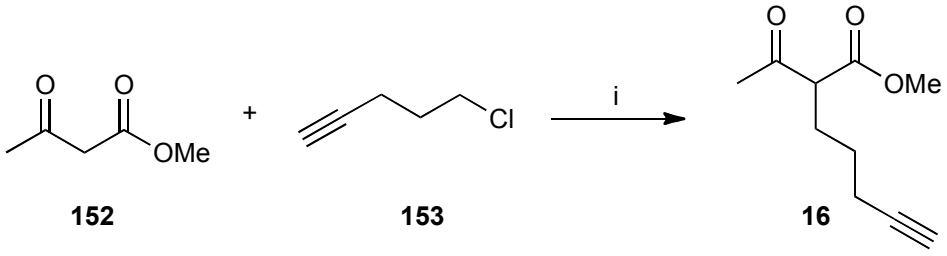
The yield of the reaction was similar to Michelet group,[46] however the time taken for the reaction to complete was much longer. The catalyst appeared air-stable and worked even in solvent without previous drying in 'open flask' conditions (Entry 3, Table 18). The enantiomeric excess was determined by HPLC. To increase association between metal-catalyst and chiral counterion non-polar solvent (benzene) was attempted (Entry 4, Table 18). The product of cycloisomerisation was formed; the yield of the reaction was still satisfactory (63%), however no optical activity was observed.

2.2.3.2 Second Generation Gold(I) Complex Based on (L)-leucine as a Catalyst in Conia-ene Reaction

The original Conia-ene reaction proceeds under thermal conditions,[29,103] however transition metal catalysts[30] such as Pd,[31] Mo [32] or Cu [33] have been used. Toste and co-workers used intramolecular Conia-ene transformation, using gold catalysis, based on a triphenylphosphine gold catalyst with success.[34,35] However the catalytic enatioselective Conia-ene reaction using chiral gold complexes based on BINAP (the structure of complexes showed in Chapter 1.4.2.2 p.48) gave good yield but without any optical activity. The authors suggest that this negative result is a consequence of linear geometry of gold(I) complexes.[104] The enantiomeric excess was obtained (up to 89% *ee*) when non-linear Pd(II) complex ((*R*)-DTBM-SEGPHOS-Pd(OTf)$_2$) was used.[104] The mechanism of the reaction involves the nucleophilic attack of the enol form of the ketoester on Au(I)-alkyne complex and was investigated by Toste.[35]

The Conia-ene reaction was chosen as the second model of transformation.

The methyl 3-oxobutanoate **152** and 5-chloropent-1-yne **153** was used to synthesise the model compound **16** according Fournet procedure (Scheme 70).[105]

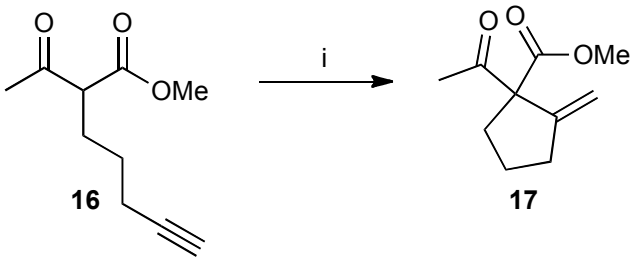


152 **153** **16**

Reagents: i) KI (0.5 eq.), NaH (1.1 eq.), THF/CH_2Cl_2, 24 h, reflux.

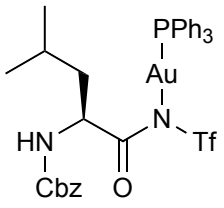
Scheme 70

The prepared starting material **16** was used in cyclisation reaction with catalyst **150** at room temperature (Scheme 71).



16 **17**

Reagents: i) 5 mol% **150**, CH_2Cl_2, 96%.



150

Scheme 71

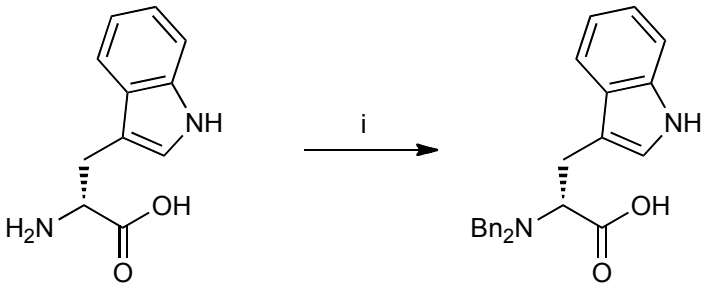
The reaction proceeded in dry dichloromethane under nitrogen over 5 days and the obtained yield of the reaction was excellent at 96%. No optical rotation $[\alpha]_D$ was observed. The results obtained showed that the chosen way is correct and the desired triflic amide can be used as a couterion. Based on that results a bulkier aminoacid was chosen as a more efficient source of chirality.

2.2.4 Protection of Amine Group on (*D*)-tryptophan

The same strategy, with a small modification (Scheme 62), which was used successfully in the preparation of gold(I) complex based on (*L*)-leucine, was chosen to prepare the new catalytic system. *N*-dibenzyl protection of aminoacid instead of using Cbz protection was attempted. The benzyl group (Bn) was used due to the high stability and difficulty of removal in base and acid condition.[92] The (*D*)-tryptophan (**131d**) (Scheme 72) was chosen as starting material due to bulky indolyl group.

The protection of amine group was prepared using the reductive amination of benzaldehyde (Scheme 72).[106] The reaction mechanism involves forming a hemiaminal, which loses a molecule of the water to form imine. Reductive agent subsequently reduces the imine.

The product of reductive animation **154** was successfully synthesised, however the yield was very low (12%) (Scheme 72).



131d **154**

a) Reagents: i) PhCHO, $Na(BH_3)CN$, phosphate buffer pH=7, 3 days, 12%.

b) Reagents: i) BnCl, K_2CO_3 aq., EtOH, reflux, 1 h, 43%.

Scheme 72

The poor yield of the reductive amination lead to change of approach. The *N,N*-dibenzylation reaction using benzyl chloride and potassium carbonate in ethanol was attempted and after 1 h of reflux, the desired compound **154** (Figure 15) was synthesised in 43% yield using Velluz's procedure.[107]

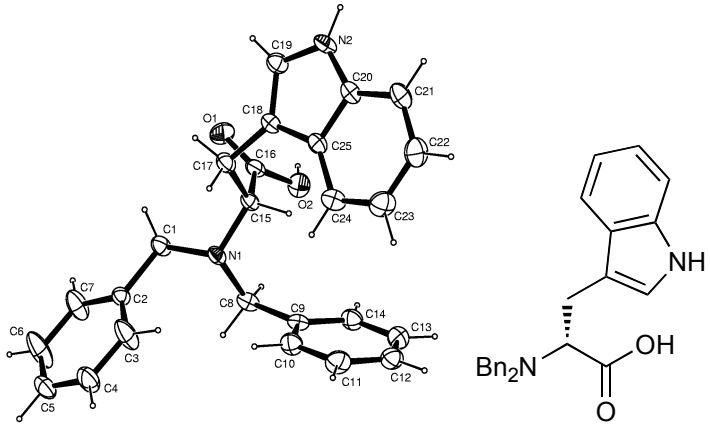
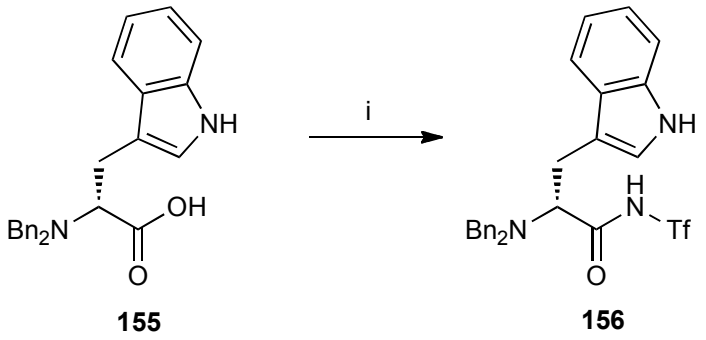


Figure 15

2.2.5 Synthesis of Triflic Amide ((*D*)-trytophan)

Based on the experience of the (*L*)-leucine amidation, the preparation of amide **156** (Scheme 73) was attempted with satisfactory yield 73% using triflic amine (**149**), $HOBt{\cdot}H_2O$, EDC in dichloromethane.



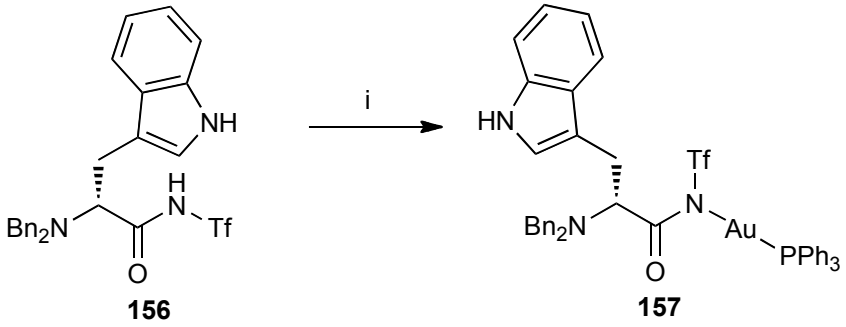
155 **156**

Reagents: i) $TfNH_2$ (**149**), HOBt H_2O, EDC, CH_2Cl_2, 3 days, 73%.

Scheme 73

2.2.6 Synthesis of Gold(I) Complex Based on (*D*)-tryptophan

The complex **157** was synthesised according the procedure used in preparation of gold(I) complex based on (*L*)-leucine using silver carbonate and Ph_3PAuCl in DCM at 0 to 10 °C (Scheme 74).



156 **157**

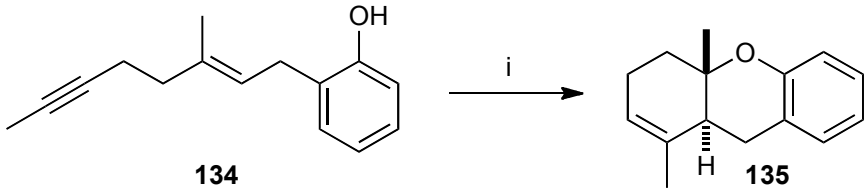
Reagents: i) Ag_2CO_3, CH_2Cl_2, 0 °C, 2 days.

Scheme 74

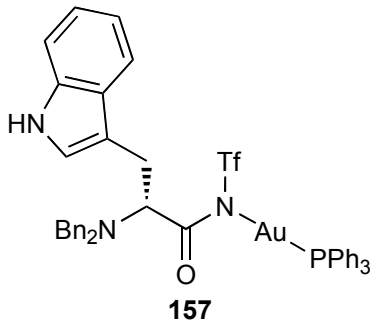
The ^{31}P NMR showed two peaks: 33.00 (s, 1), 29.92 (s, 11). The ratio between peaks showed around 9% impurity (based on ^{31}P NMR with 5 s relaxation time). Simple combination of triphenylphosphine gold chloride with the catalyst proved that the impurity was not Ph_3PAuCl (33.2 ppm). The crystallisation of the gold(I) complex was attempted using a slow diffusion method with variety of solvents and temperatures however crystals were not obtained.

2.2.7 Second Generation Gold(I) Complex Based on (*D*)-tryptophan as a Catalysts in Cycloisomerisation

The intramolecular phenoxycyclisation reaction on 1,5-enyne was attempted with gold(I) complex **157** using (*E*)-2-(3'-methyloct-2'-en-6'-ynyl)-phenol **134**, previously synthetised, as a model starting material (Scheme 75). The reactions were performed under nitrogen with 0.5 M concentration in dichloromethane at room temperature during 5 days with 5 mol% of **157**.



Reagents: i) 5 mol% **157**, CH_2Cl_2, 5 days, RT, 46%.



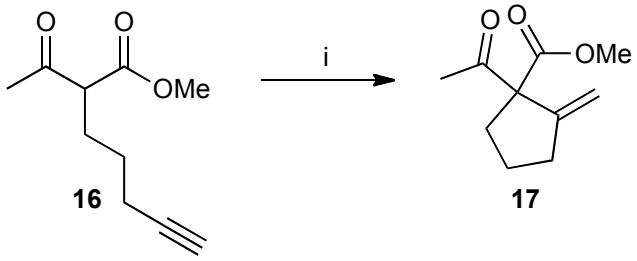
Scheme 75

The cyclisation product **135** was obtained in 46% yield. The enantiomeric excess has been check on HPLC with a chiral column and an only racemic mixture was observed. The catalyst, surprisingly, appeared to be less active than gold(I) complex **150**.

2.2.8 Second Generation Gold(I) Complex Based on (*D*)-tryptophan as a Catalyst in Conia-ene Reaction

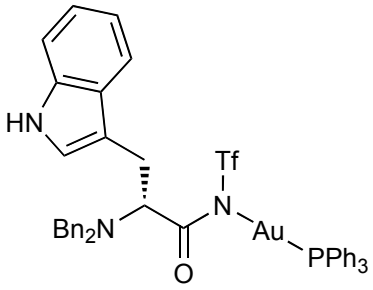
The second model reaction Conia-ene was attempted with gold(I) complex **157**. The reaction was conducted in dry dichloromethane, under nitrogen using the previously synthesised starting material **16** (Scheme 76). According to previous results with 1,5-enyne, the new catalyst **157** appeared to be less active. The reaction was controlled by

TLC and performed longer than 5 days to achieve a better yield. The reaction was stopped after 7 days, and the yield reached 90%. The optical rotation was determined by polarimeter, however a racemic mixture of product **17** was obtained.



16 **17**

Reagents: i) 5 mol% **157**, CH_2Cl_2, 90%.



157

Scheme 76

2.2.9 Conclusion

The two new gold(I) complexes showed catalytic activity. The compounds appeared to be stable and storable. Even after 1 year in the freezer at -25 °C under nitrogen they did not lose their catalytic properties, however in the attempted reactions they did not introduce chirality to the product. It is possible that the nature of these transformations would not let introduction of chirality to the product with these kinds of catalysts. In literature, only examples of the hydroalkoxylation,[67] hydroamination[66] and hydrocarboxylation[66,68,69] of allene were conducted with chiral counterion catalysts with positive results. The newly introduced chiral centre is generated very close to the chiral complex, unlike a Conia-ene cyclopentannulation, which can result in a racemic mixture.

Both complexes are based on the triphenylphosphine gold compound, which means that the electronic effect from the L-ligand side is the same. The amide part of the counterion in both cases is the same, which suggest that activity of both compounds

should be the same. However, the results showed different the activity between the two catalysts, which provides the possibility that the 'amine' part of the counterion has an influence on reactivity (Figure 16).

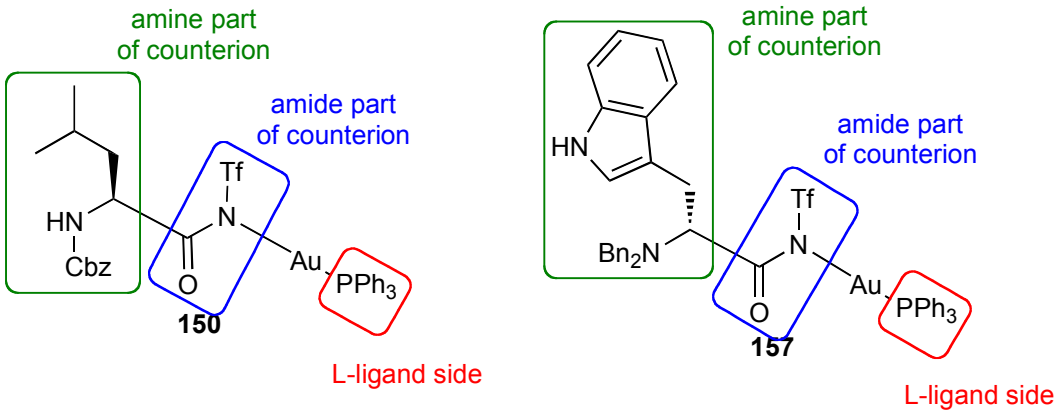
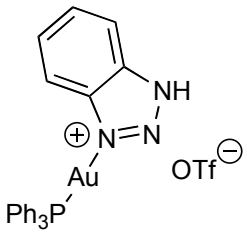


Figure 16

2.3 Rationalisation

The first generation of gold(I) complexes did not show any catalytic activity. The cause of their unreactivity could be due to the stability of the gold-compounds, which can be explained by the degree of covalence in Au-X bond using the ^{31}P NMR spectroscopic shift as proposed by Shi.[108,109] According to this theory, PPh_3AuCl with a phosphorous signal 34.31 ppm referenced to H_3PO_4 (33.20 ppm was found during our research) shows no catalytic activity or high stability, which suggests that Au-Cl bond is mostly covalent. On the other hand highly reactive PPh_3AuOTf with phosphorus signal 28.80 ppm in which the character of Au-OTf the bond can be attributed as highly ionic. The highly reactive and stable Gagosz catalyst has shown a ^{31}P NMR signal of 31.6 ppm referenced to H_3PO_4 (30.60 ppm was found during our research). Similarly, the gold(I) triazole compound **158** (Figure 17) reported by Shi,[108] it has a ^{31}P NMR signal of 30.9 ppm and is also stable. Compound **158** also appears to show higher reactivity than the catalyst **30** (Gagosz catalyst), with regards to the internal alkyne hydroamination reaction at 80 °C. The phosphorous signals for our gold(I) compounds are in the range of 31.01 to 31.57 ppm. It is clearly visible, that gold compounds are out of the range 30.6 ppm corresponding to **30** (Gagosz catalyst), which suggest rather covalent character of the bond between Au and nitrogen in aminoester species. The gold compounds were very stable and the likely cationic gold species was not formed during the reaction.



^{31}P NMR = 30.9 ppm

158

Figure 17

In the second generation of gold(I) complexes the range of 29.92 ppm for compound **157** (based on (*D*)-tryptophan) and 30.6 ppm for compound **150** (based on (*L*)-tyrosine) suggest that the bond between Au and the counterion has cationic character therefore the desired compound should have catalytic properties according to Shi theory.[108] Both of the compounds showed catalytic activity, which is in agreement with Shi theory, however chirality was not introduced to the products.

2.4 Third generation gold(I) complexes (bidentate)

The previous work showed that the bond between Au-NTf R^1 (where R^1 was ester part of aminoester) can not be cationic enough (first generation gold(I) complexes) (Figure 18).

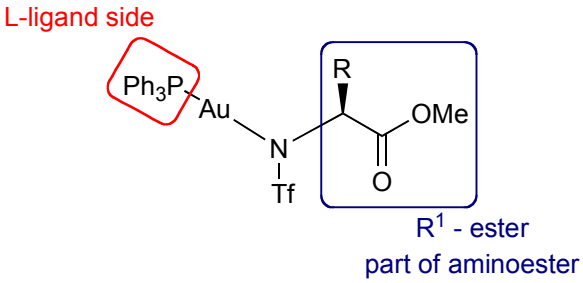


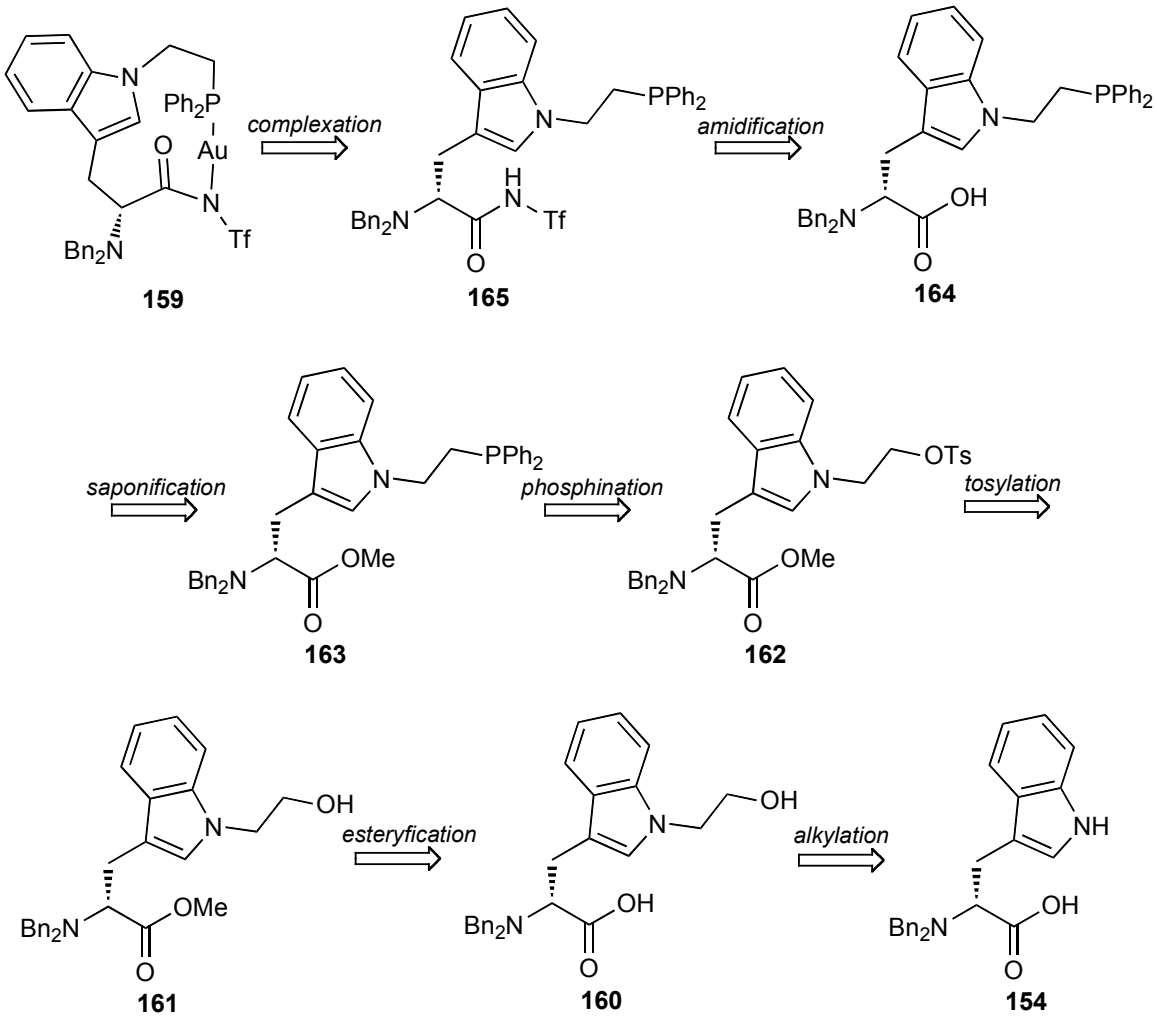
Figure 18

According to Shi's theory described above, the ^{31}P NMR shift of the first generation of gold(I) complexes were in the covalent, low activity part of the scale (the range 31.01 to 31.57 ppm). The modification of the chiral counterion, through the amidification of the acid part of amino acid with NH_2Tf, led to the invention of a new counterion pattern within the chiral part (second generation gold(I) complexes) and active catalysts (however without chiral induction to the product) (Figure 16, p. 80).

The new attempt for a chiral catalyst was performed where one of the phenyl group in triphenylphosphine can be changed to a group bearing *N*-triflic amide linkage to gold. This idea can result in a new version of catalyst where the two ideas would be combined into one: chiral L ligand and chiral X ligand. The strong preference of gold(I) species to form a linear geometry and the fact that Au-X bond should be the most labile bond, forces to synthesise the proper size cycle to avoid the possibility of dimerisation, otherwise the cycle will not form. The DFT optimization showed that the minimum ring size that allowed having the correct linear geometry of P-Au-NTf is a 9 membered cycle.[110]

2.4.1 Attempt to Synthesis Bidentate Gold(I) Complex Based on (*D*)-tryptophan

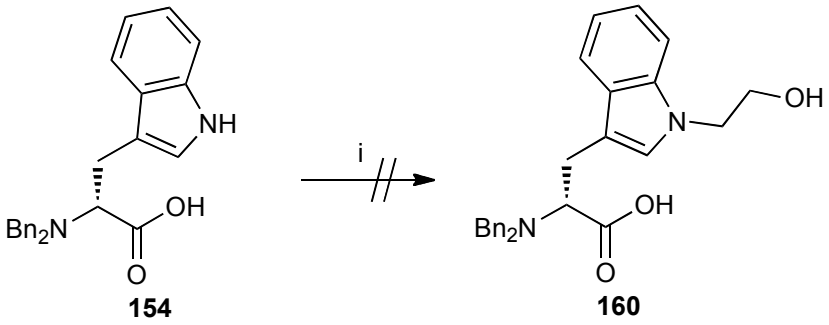
It was decided that in the new bidentate gold(I) complex the source of chirality and at the same time starting material would be (*D*)-tryptophan. Based on the knowledge from the computational experiments that, to be able to have the correct linear geometry of P-Au-NTf, the size of the cycle should not be less than a 9 membered ring.[110] The bidentate gold(I) complex **159** was designed and the retrosynthetic analysis with optimal disconnections was prepared and presented on Scheme 77.



Scheme 77

The aim was to construct a bidentate ligand based on *N,N*-dibenzyl (*D*)-tryptophan **154**, previously successfully synthetised. Through the initial disconnection follows the alkylation of **154** with 2-bromoethanol to obtain the *N*-substituted indole derivative (**160**). The conventional esterification (prepared in methanol to avoid transesterification) can protect the acid group (**161**). The compound **162** can be synthetised by a simple tosylation reaction in the presence of an amine base. The tosylation converts the alcohol group to a good living group, which can undergo a S_N2 reaction with $LiPPh_2$ to give the compound **163**. The saponification reaction followed acidic work-up can release the free acid **164**, which can then be converted in the amidation reaction to an amide **165**. The requisite gold(I) **159** can be synthesised using dimethyl sulfide gold chloride in one pot reaction with silver salt.

Various conditions were attempted to convert *N,N*-dibenzyl (*D*)-tryptophan **154** to *N*-substituted indole derivative (**160**) (Scheme 78, Table 19) using the procedures used in synthesis of *N*-substituted indoles and pyrrolidinones,[111-114] but all failed to give the expected compound.



Reagents: i) solvent and condition - see Table below

Scheme 78

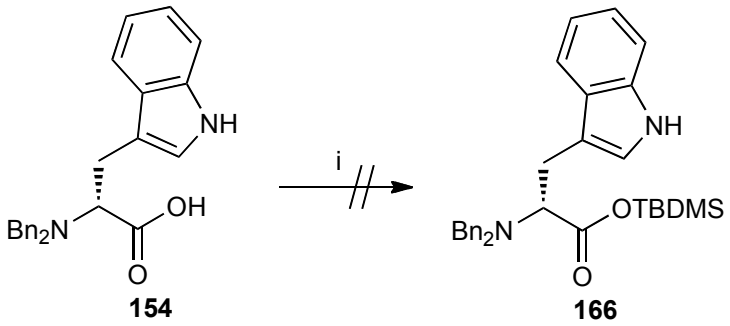
Table 19

Entry	Solvent	Alkylating agent	Base	T [°C]	Additive	Results
1	THF	$Br(CH_2)_2OH$	NaH	0		/[a]
2	THF	$Br(CH_2)_2OH$	KOH	RT	Bu_4NBr	/[b, c]
3	THF	$Br(CH_2)_2OTMS$	NaH	0		/[b]
4	DMF	$Br(CH_2)_2OH$	NaH	0		/[b]
5	Toluene	$Br(CH_2)_2OH$	KOH	RT	TDA-1	/[b]
6	DMSO	$Br(CH_2)_2OH$	KOH	RT		/[b]
7	MeCN	$Br(CH_2)_2OH$	KOH	RT	TDA-1	/[b]

(a) Unidentified products; (b) Recovered starting material; (c) Reaction sonicated 3 h.

In the prepared reactions the temperature was the limitation due to esterification at higher temperature (esterification product was observed when reaction was proceeded in acetonitrile under reflux in the presence of potassium hydroxide and TDA-1). For this reason, the reactions was performed at 0 °C and room temperature. To avoid esterification at higher temperatures, the acid group needs to be protected. In retrosynthetic analysis, the

esterification reaction was planned, however at this stage, this kind of protection could result in transesterification. The TBDMS group was chosen due to high stability. The protection of acid was attempted using TBDMSCl, imidazole in dimethylformamide at room temperature using the Corey procedure,[115] however the desired compound **166** was not achieved (Scheme 79) and only starting material was recovered.



Reagents: i) TBDMSCl, imidazole, DMF, RT.

Scheme 79

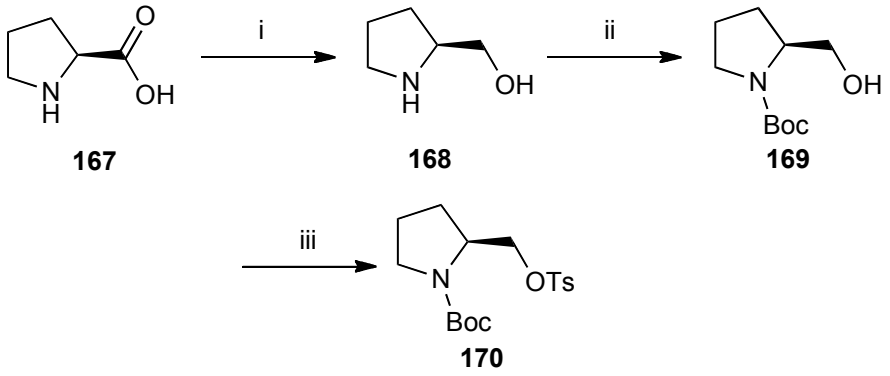
2.4.2 Synthesis of Gold(I) Complex Based on (*L*)-prolinol

Due to previous negative results with *N,N*-dibenzyl (*D*)-tryptophan **154** (Scheme 79), the new route was attempted to prepare bidentate gold(I) complexes. The (*L*)-proline was chosen as a source of chirality and starting material, which can be converted to a chiral phosphine.

2.4.2.1 Reported Route to Chiral Phosphines Based on (L)-prolinol

The methodology of the preparation of the chiral phosphine with (*L*)-prolinyl group was based on Tomioka's report.[116]

The Boyle procedure was used to reduce (*L*)-proline **167** to (*L*)-prolinol **168** using lithium aluminium hydride in tetrahydrofuran in 82% yield (Scheme 80).[117] The protection of nitrogen in **168** was prepared according to the Spatola procedure using *di-tert*-butyldicarbonate in ethyl acetate, in en excellent 96% yield of compound **169** (Scheme 80).[118] The tosylation reaction was prepared according to the Lee procedure.[119]



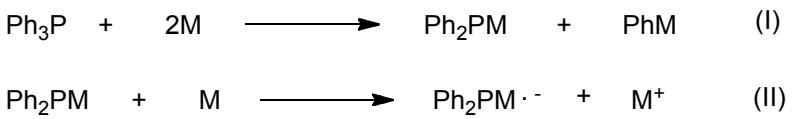
167 **168** **169** **170**

Reagents: i) $LiAlH_4$,THF, 0 ^oC to RT, 24 h, 82%; ii) $(Boc)_2O$, AcOEt, RT, 96%; iii) TsCl, pyridine, CH_2Cl_2, 66%.

Scheme 80

The next step was the preparation of the chiral phosphine. In the literature, the introduction of the diphenylphosphine group to aryl[120] or alkyl[121] were described. All of the transformations were based on the nucleophilic substitution reaction of diphenylphosphine nucleophile, which attacks substrate to create a new bond while the leaving group (LG) departs with an electron pair. The diphenylphospine nucleophile can be prepared from chlorodiphenylphosphine with alkali metal,[121-123] diphenylphosphine with a base[120] or triphenylphosphine in presence of alkali metals.[124-126] Tomioka, in his synthesis, used chlorodiphenylphosphine in the presence of sodium metal in dioxane/tetrahydrofurane with tosylated *N*-Boc prolinol **170** in 77% yield.[116,122]

In 1965, Kaiser studied the reaction of the triphenylphosphine with alkali metals as a function of the concentration, and it was found that the reaction goes through two steps: the first step (I) is a C-C cleavage rather then formation of the triphenylphosphine negative ion, the second step (II) is the radical formation of $Ph_2PM^{\bullet -}$ **(**where M = K, Na or Li) when the metal reduced previously produced the metal diphenylphosphine (Scheme 81).[124]

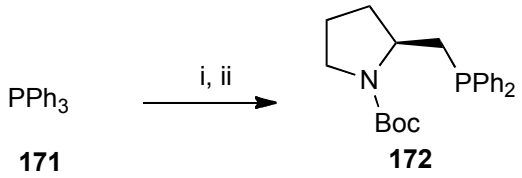


Scheme 81

The procedure of the preparation of **172** (Scheme 82) was modified and instead of chlorodiphenylphosphine according to Tomioka, triphenylphosphine was used with

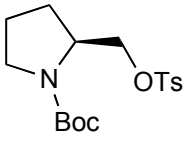
lithium metal in dry tetrahydrofuran at room temperature under argon (the dissolution of lithium metal was an indication of ending of the reaction).[120,126]

The reaction of triphenylphosphine **171** with lithium metal gives the side product, which is phenyllithium. The phenyllithium was expected to be a stronger base than diphenylphosphine lithium, as described in literature that diphenylphosphine reacted with phenyllithium to produce lithium diphenylphosphide and benzene.[127] During the addition of *N*-Boc tosylated prolinol **170** possible competition between phenyllithium and diphenylphosphine could occur, however the phenyl product was not observed and desired product **172** was obtained in 60% yield (Scheme 82). This result may readily explain that lithium diphenylphosphide appeared to be a better nucleophile then phenyllithium.



171 **172**

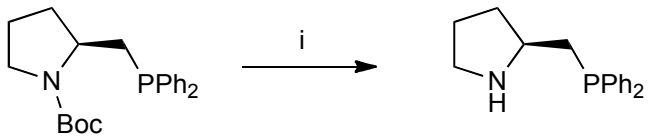
Reagents: i) Li, THF, RT; ii) **170**, RT, 60%.



170

Scheme 82

Many methods of the cleavage of the Boc protecting group was reported in literature[128] however two methods were commonly used. The first method is a deprotection with an acid such as trifluoroacetic acid, and the second used a smaller quantity of stronger inorganic acid such as hydrochloric acid.[128-131] Tomioka in his synthesis of chiral phosphine **173**, used trifluoroacetic acid for the deprotection.[116]

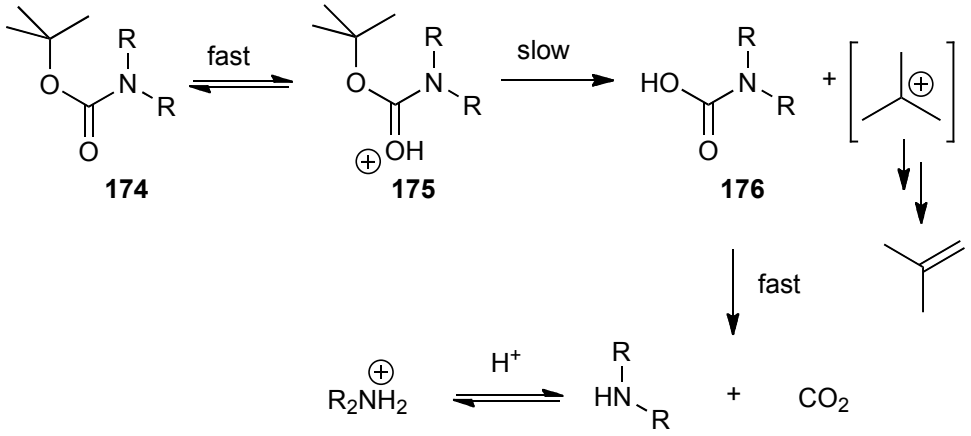


172 **173**

Reagents: i) CF_3COOH, CH_2Cl_2, 99%.

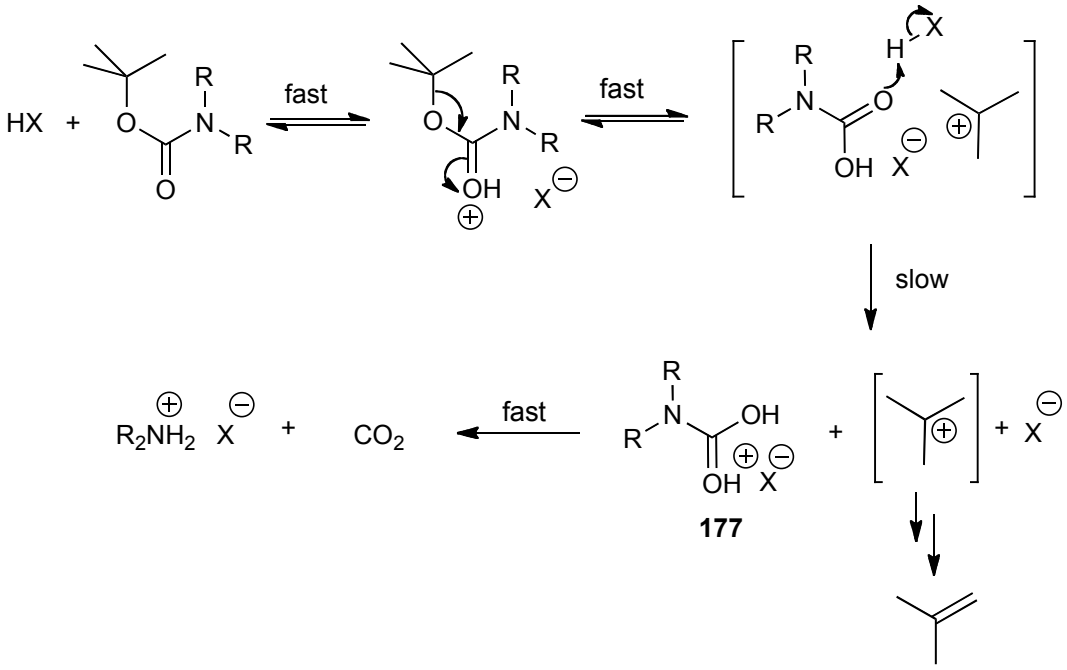
Scheme 83

The same acidic procedure was repeated and gave an excellent 99% yield. Ashworth studied the kinetics and mechanism of *N*-Boc cleavage in acidic condition.[132] The widely accepted mechanism of the acid-catalysed deprotection of Boc-protected amine (**174**) is a rapid, reversible protonation of the Boc group (**175**), followed by slow fragmentation of the protonated intermediate[133] to *tert*-butyl cation (with further elimination of a proton) and carbonic acid (**176**), which undergoes further fast decomposition by decarboxylation (Scheme 84).[134]



Scheme 84

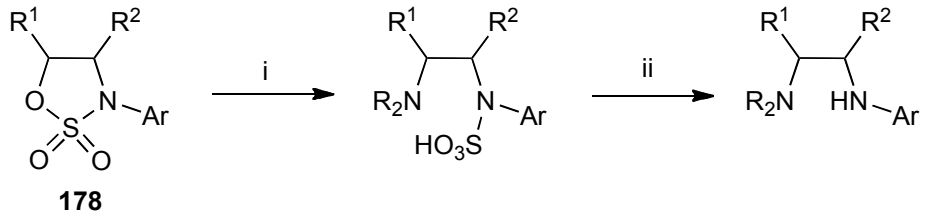
Ashworth, based on collected data, proposed a new mechanism of *N*-Boc cleavage *via* the general acid-catalysed separation of ion-molecule pair resulting from the fragmentation of the intermediate ion pair **177** (Scheme 85).[132]



Scheme 85

2.4.2.2 Novel Route to Chiral Phosphine Based on (L)-prolinol

Cyclic sulfamidates as well as cyclic sulfites and cyclic sulfates can react with many different nucleophiles.[135] In 1986, Zubovics reported nucleophilic substitution of sulfamidates **178** at the carbon bearing the oxygen with secondary amines under harsh reaction conditions (Scheme 86).[136]



178

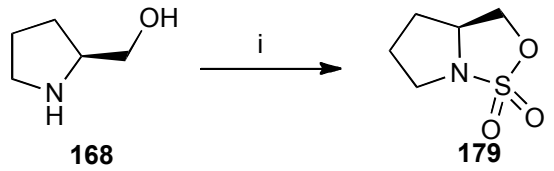
Reagents: i) R_2NH, EtOH, 130 ^oC; ii) NaOH aq

Scheme 86

One year later McGregor reported the substitution of methanol and secondary amines on the sulphonamide derived for of *S*-prolinol in the presence of a catalytic amount of trifluoroacetic acid.[137] However, attempts to react the sulfonamide of *S*-prolinol with anionic nucleophile such as MeMgBr, PhLi or MeONa under a wide variety of condition failed.

Based on the results of Zubovics[136] and McGregor,[137] it was decided that this transformation could be useful for the preparation of chiral phosphine **173**. In the literature two processes were found of the preparation of cyclic sulfonamidite **179**. In the stepwise approach, the aminoalcohol reacts with thionyl chlorides, which yields the cyclic sulfonamidite, followed by oxidation with ruthenium tetroxide[138-142] or potassium permanganate.[136] In the second method, the straightforward preparation of sulfonamidate ester of *S*-prolinol was using sulfuryl chloride.[137]

The direct method of preparation sulfonamidate ester of (*L*)-prolinol **168** was chosen, following the McGregor procedure (Scheme 87). After 15 h only product was observed by TLC, however after purification *via* column chromatography the desired product was obtained in 30% yield. The result suggests that the product is unstable on the column or decomposition occurred during the acidic work-up, however this was not proven.

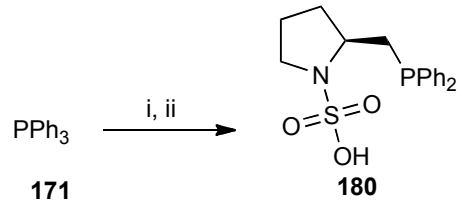


168 **179**

Reagents: i) SO_2Cl_2, Et_3N, CH_2Cl_2, 30%

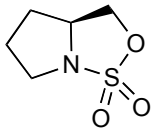
Scheme 87

In the next step triphenylphosphine **171** (Scheme 88) was transferred to lithium diphenylphosphine salt in dry tetrahydrofuran in the presence of two equivalent of metal lithium at room temperature under argon. The solution of sulfonamidate ester of (*L*)-prolinol **179** (Scheme 88) in terahydrofuran was added and after 20 minutes the starting sulfonamidate ester of (*L*)-prolinol **179** was not observed. The desired product **180** was obtained in 91% yield.



171 **180**

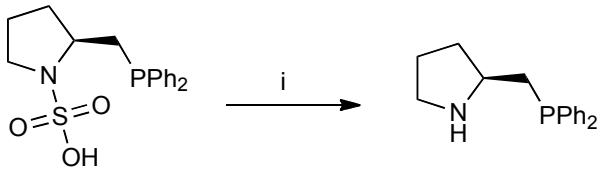
Reagents: i) Li, THF, R.T.; ii) **xx**, RT, 91%



179

Scheme 88

The hydrolysis of sulfate can be carried out in acidic[140,141,143-145] or basic conditions.[136,137] Various conditions were attempted to hydrolyse sulfate **180** (Scheme 89, Table 20).



180 **173**

Reagents: i) see Table below

Scheme 89

Table 20

Entry	Condition	T [°C]	Time [h]	Yield [%]
1	2M NaOH	90	24	/[a]
2	3M HCl	RT	17	/[a]
3	5M HCl	RT	2	/[a]
4	10% H_2SO_4/CH_2Cl_2	RT	24	/[a]
5	30% H_2SO_4	100	24	/[a]
6	32% HCl	RT	24	/[a]
7	32% HCl[b]	100	17	65

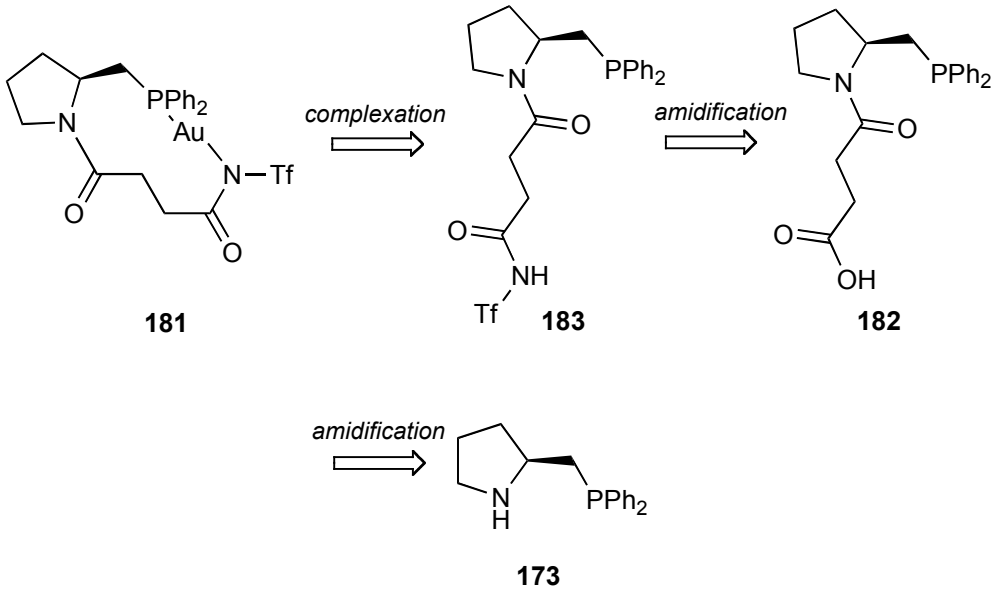
(a) Recovered starting material; (b) 32% HCl was deoxygenated before the use to avoid phosphine oxidation.

During the investigation of acidic condition reaction it was found that the hydrolysis of the sulfate group could be achieved in degassed 32% hydrochloric acid (to avoid phosphine oxidation) at 100 °C in 65% yield (Entry 7, Table 20).

The new way involving concomitant protection of nitrogen with conversion of hydroxyl group into a leaving group gave a shorter route to prepare chiral phosphine **173**.

2.4.2.3 Attempt to Synthesis Gold(I) Complex Based on (L)-prolinol with 'Rigid Connection' Between (L)-prolinyl Moiety and Chain

The computation experiments prepared before showed that to allow having the correct linear geometry of L-Au-X the size of the cycle should not be less than a 9 membered ring.[110] A retrosynthetic analysis is presented on Scheme 90.



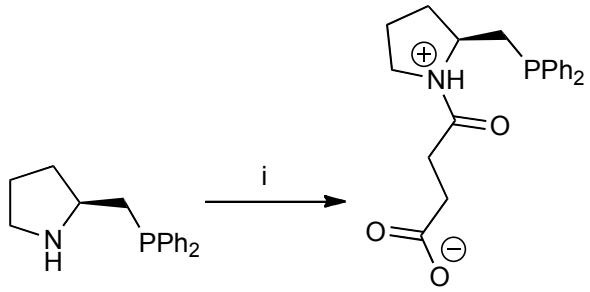
Scheme 90

The aim of this approach was to construct a cyclic gold(I) complex **181** based on the previous synthesised phosphine **173** (Scheme 90). The compound **182** can be prepared by an amidification with succinic anhydride. The amide bond can prevent rotation of the chain. The second amidification reaction should allow for formation of compound **183** by utilising triflic amine **149**. The requisite gold(I) **181** can be synthesised using dimethyl sulfide gold chloride in one pot reaction with silver salt.

The reaction of amine with cyclic acid anhydride is one of the methods of amide formation widely used in peptide synthesis.[146-148] This methodology was adapted to the

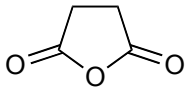
synthesis of compound **182**. Succinic anhydride is the reagent of choice for the amidification reaction in the presence of triethyl amine and catalytic amount of 4-DMAP, which is used as a catalyst in Steglich estryfication.[84] The mechanism of the amidation reaction involves nucleophilic substitution of 4-DMAP at the carbonyl group of anhydride, leading to a reactive amide, which reacts rapidly with an amine. 4-DMAP reacts as an acyl transfer agent.

The reaction of phosphine **173** with succinic anhydride **184** was performed in dichloromethane and yielded 79% (Scheme 91). The ^{1}H NMR showed two rotamers with ratio 1:2.96.



173 **182**

Reagents: i) **184**, 4-DMAP, CH_2Cl_2, 79%.



184

Scheme 91

The structure of the desired product **182** was confirmed by X-ray diffraction (Figure 18).

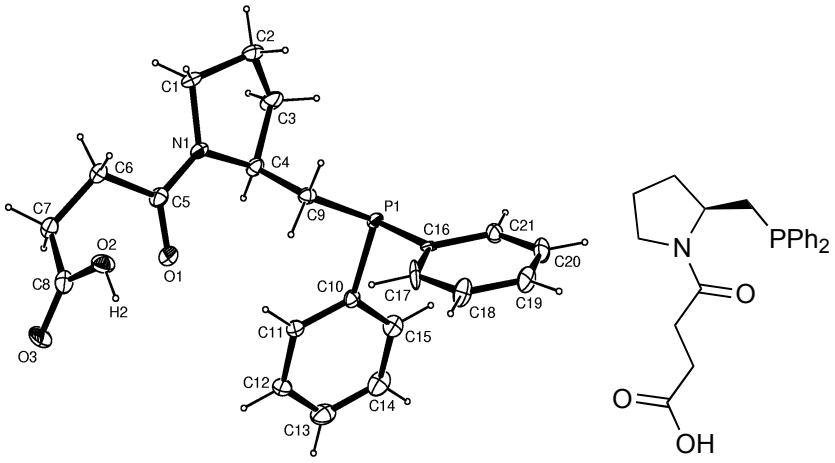
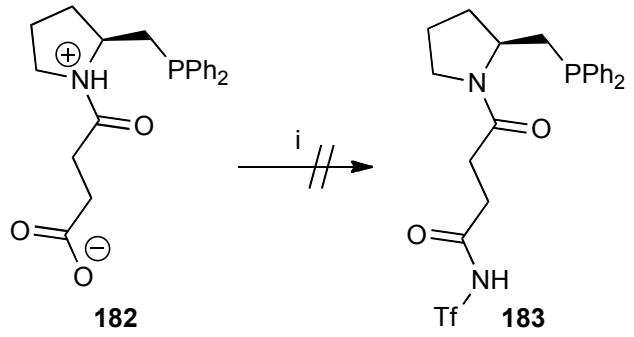


Figure 18

The next step was the synthesis of triflic amide **183** (Scheme 92). Various conditions were attempted to convert compound **182** to triflic amide derivative (**183**) using direct method of amidation with coupling agents (Entry 1 - 5, Table 21) or step method involving preparation of acid chloride followed substitution of triflic amine (Entry 6 – 13, Table 21), but all failed to give the expected compound.[94,96,149-154]



182 **183**

Reagents: i) see Table below

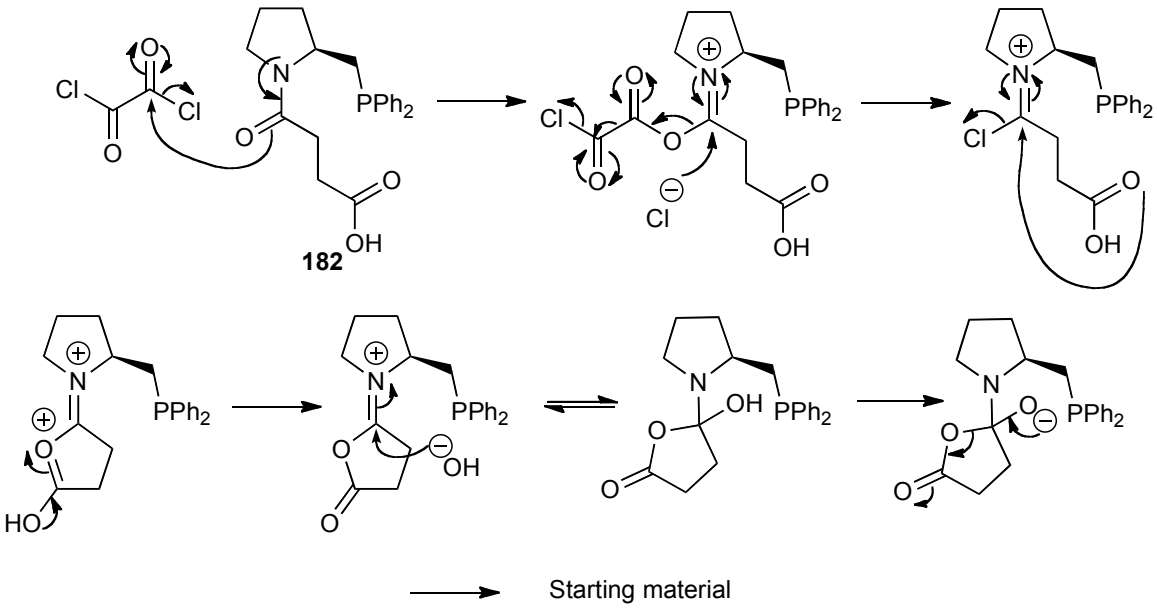
Scheme 92

Table 21

Entry	Step I	Step II	Solvent I	Solvent II	T^{I} [°C]	T^{II} [°C]	Results
1	EDC, H_2NTf	-	DCM	-	0 to RT	-	/[a]
2	HOBt·H_2O, EDC, H_2NTf	-	DCM	-	0 to RT	-	/[a]
3	EDC, 4-DMAP, H_2NTf	-	DCM	-	0 to RT	-	/[b]
4	CDI, H_2NTf	-	THF	-	RT	-	/[b]
5	DDC, H_2NTf	-	THF	-	RT	-	/[a]
6	$(COCl)_2$, DMF(1drop)	H_2NTf, 2,6-lutidine	DCM	DCM	0 to RT	0 to RT	/[a]
7	$(COCl)_2$, DMF(1drop)	H_2NTf, Et_3N	DCM	Et_2O	0 to RT	0 to RT	/[a]
8	$(COCl)_2$, DMF(1drop)	H_2NTf, Et_3N	DCM	DCM	0 to RT	0 to RT	/[a]
9	$(COCl)_2$, DMF(1drop)	2 eq. H_2NTf, Et_3N	DCM	DCM	0 to RT	0	/[a]
10	$(COCl)_2$, DMF(1drop)	H_2NTf, NaH	DCM	THF	0 to RT	RT	/[a]
11	$SOCl_2$	H_2NTf, Et_3N	Et_2O	DCM	0 to RT	0	/[b]
12	Vilsmeier reagent	H_2NTf, Et_3N	DCM	DCM	RT	RT	/[a]
13	MeOCOCl, Et_3N	H_2NTf, Et_3N	DCM/ dioxane	DCM/ dioxane	-10 ÷ -5	RT	/[a]

(a) Starting material recovered partially; (b) Starting material was not recovered.

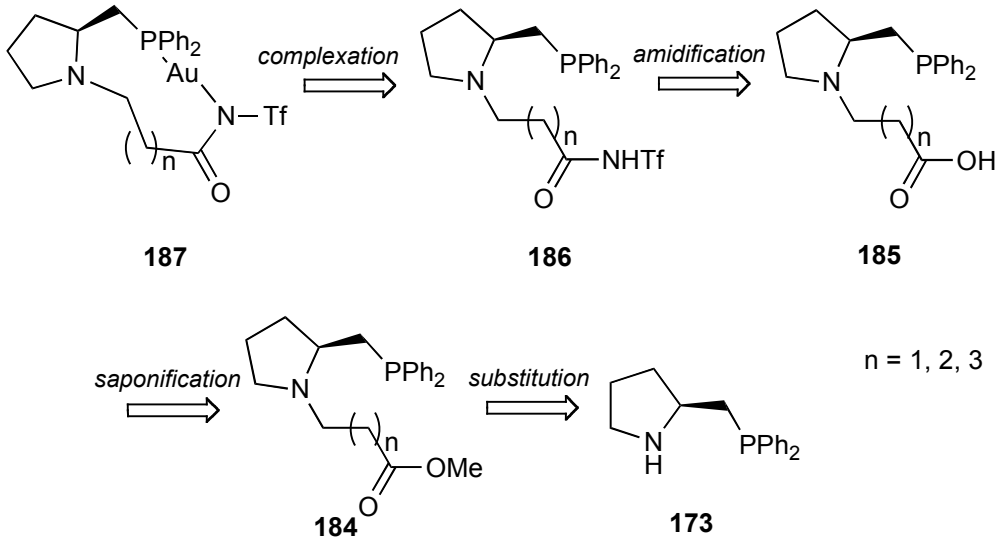
The possible explanation of recovering of the starting material is caused by chlorinating agent, which probably attacks the amide bond (Scheme 93). Further investigation will show that the removal of the carbonyl group affects the reactivity.



Scheme 93

2.4.2.4 Synthesis Gold(I) Complex Based on (L)-prolinol with 'Flexible Connection' Between (L)-prolinyl Group and Chain

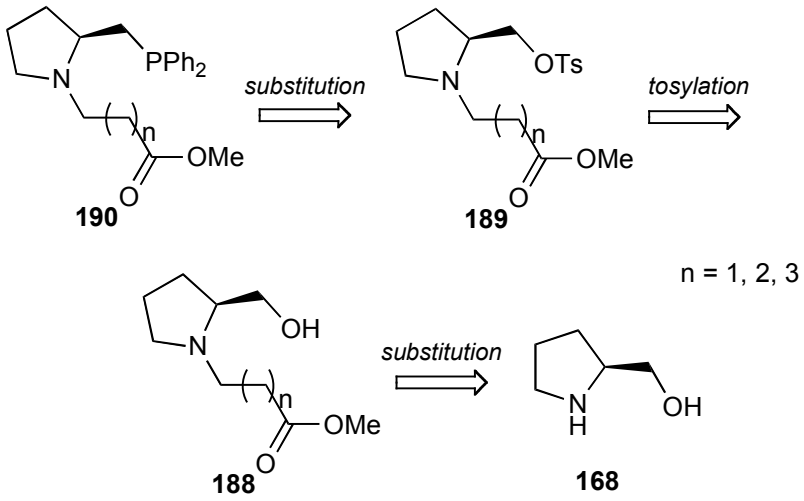
The initial strategy for the synthesis of the triflic amide **183** with a 'rigid connection' between (*L*)-prolinyl group and the chain failed (Scheme 92). The analysis of the previous attempts suggests that the amide group could cause the problem. It was decided that the carbonyl group next to the nitrogen should be removed and a new synthetic route was planned (Scheme 94).



Scheme 94

Compound **184** (Scheme 94) can be prepared by alkylation of the amine at a chiral phosphine **173** with alkyl halide by nucleophilic aliphatic substitution. The ester **184** can be saponified followed an acidic work-up to obtain the corresponding acid **185**. The amidification reaction can convert acid **185** to triflic amide **186**. The requisite gold(I) **187** can be synthesised using dimethyl sulfide gold chloride in a one pot reaction with a silver salt. The advantage of this approach is that different sizes of chain can be used, which can give the possibility of establishing in practice the correct size of cycle in bidentate gold(I) complex.

The second alternative method of preparation of bidentate gold(I) complex (Scheme 95) could be achieved directly from (*L*)-prolinol **168**, which could be *N*-alkylated. The *N*-alkylation would be equivalent to protection of the nitrogen in the previous route with Boc. The desired compound **188** could be tosylated to compound **189** and transformed with diphenylphosphine lithium salt in S_N2 reaction to chiral phosphine **190**. The rest of the route could be achieved from the appropriate step showed in Scheme 94.



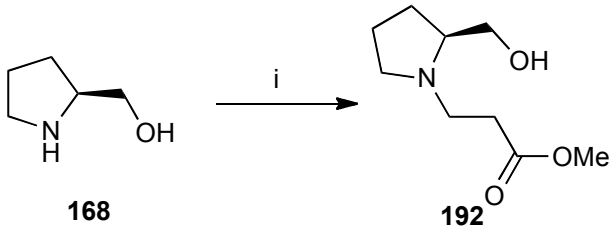
Scheme 95

2.4.2.4.1 Attempt to Synthesis (L)-methyl 3-(2-((diphenylphosphino)methyl) pyrrolidin-1-yl)propanoate Through 'Direct Alkylation'- Shorter Method

The *N*-alkylation reaction is a common route to higher-substituted amines.[155-158] The secondary amine is converted to tertiary amine under mild conditions; however, the

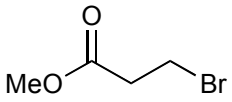
alkylation of a primary amine can cause problems due to the nucleophilic of secondary amines, which will react preferentially with alkylating agent.

The *N*-alkylation reaction of (*L*)-prolinol **168** was achieved with methyl 3-bromopropionate **191** in the presence of triethylamine in 72% yield (Scheme 96).



168 **192**

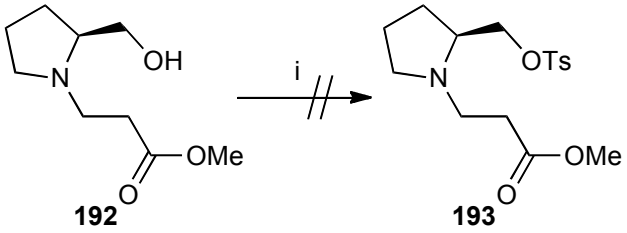
Reagents: i) **191**, Et_3N, CH_2Cl_2, 30 ^oC, 72%.



191

Scheme 96

Three methods of tosylation were attempted to synthesise tosylated *N*-substituted (*L*)-prolinol **193** from *N*-substituted (*L*)-prolinol **192** (Scheme 97, Table 22) but all failed to give the expected product and only starting material was recovered.[118,119]



192 **193**

Reagents: i) see Table below

Scheme 97

Table 22

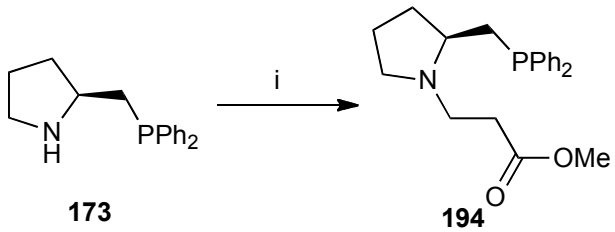
Entry	Condition	Additive	T[°C]	Solvent	Result
1	TsCl, pyridine	-	0 to RT	DCM	/[a]
2	TsCl	4-DMAP	0 to RT	DMF	/[a]
3	TsCl, Et_3N	4-DMAP	0 to RT	DCM	/[a]

(a) Starting material recovered.

2.4.2.4.2 Synthesis of (L)-methyl-3-(2-((diphenylphosphino)methyl)pyrrolidin-1-propanoate

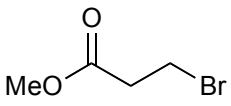
The shorter route to chiral phosphine **190** (Scheme 95, page 97) failed on the tosylation step. It was decided to use the longer method described on page 96.

The *N*-alkylation of compound **173** was achieved with methyl 3-bromopropionate **191** in dichloromethane in the presence of triethylamine in 47% yield of desired product **194** (Scheme 98) according to Gurney's procedure.[159]



173 **194**

Reagents: i) **191**, Et_3N, CH_2Cl_2, 30 ^oC, 47%.

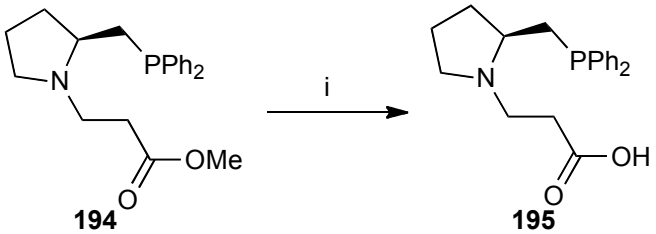


191

Scheme 98

2.4.2.4.3 Synthesis of (L)-3-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)propanoic acid

The saponification reaction[160] followed acidic work-up was used for preparation of acid **195** in quantitative yield (Scheme 99).[161] A more direct method of preparation of acid **195** in solution of 32% hydrochloric acid/*p*-dioxane (1:1) at 60 °C was not successful.[159] Only unrecognised products were achieved.



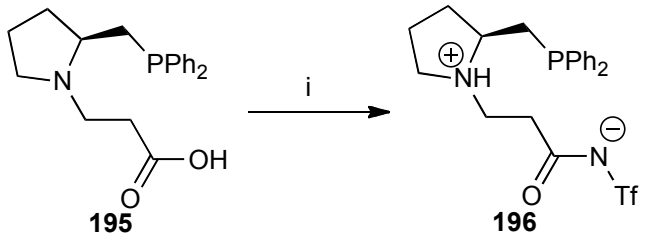
194 **195**

Reagents: i) 1 M NaOH, MeOH, RT, quantitive yield

Scheme 99

2.4.2.4.4 Synthesis of (L)-3-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-N-((trifluoromethyl)sulfonyl)propanamide

A direct amide formation successfully used in the preparation of the second generation of gold(I) complexes was chosen to synthesise triflic amide **196**. The acid **195** was converted to triflic amide **196** in the presence of EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) and HOBt·H_2O (HOBt = hydroxybenzotriazole) in dichloromethane and gave compound **196** in 49% yield (Scheme 100).[96]



Reagents: i) **150**, HOBt*H_2O, EDC, CH_2Cl_2, 0 °C - RT, 49%

Scheme 100

The desired product **196** was confirmed by X-ray diffraction (Figure 19).

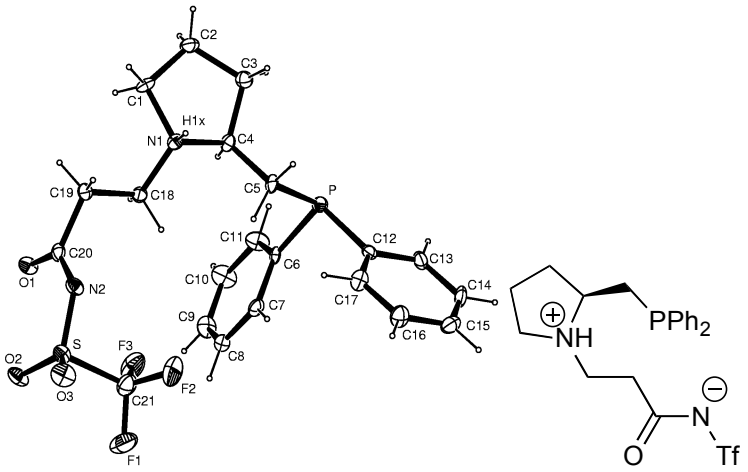
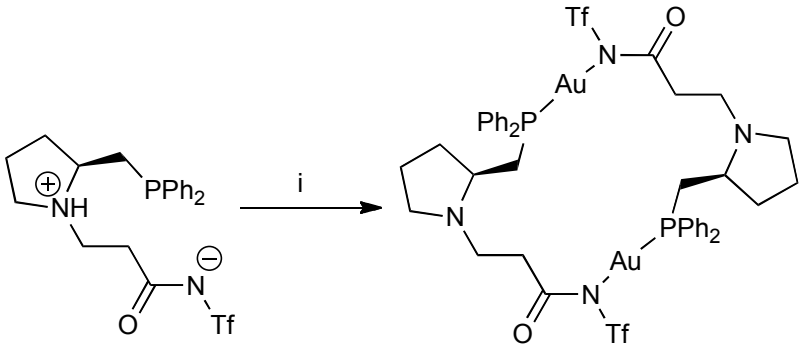


Figure 19

2.4.2.4.5 Synthesis of Third Generation Gold(I) Complex

The formation of desired bidentate gold(I) complex **197** (Scheme 101) required a stoichiometric amount of commercially available dimethylsulfide gold chloride. The required dimethylsulfide gold chloride can be easily synthetised from gold metal according to the procedure of Puddephatt in 92% yield.[162] The synthesis of bidentate gold(I) complex was attempted with triflic amide **196** in dichloromethane with

dimethylsulfide gold chloride in the presence of silver carbonate (Scheme 101). The product was crystallised upon slow diffusion of pentane (very small crystals) or benzene into a solution of the gold(I) complex in dichloromethane. X-ray diffraction studies revealed dimer complex **197** (Scheme 101, Figure 20). The ^{31}P NMR showed two peaks with chemical shifts, 21.92 (s), 20.81 (s) ppm and high-resolution mass spectroscopy showed only mass of dimer (no mass of monomer). The analysis of X-ray data revealed that molecule is not symmetrical and showed different angles between N-Au-P (177.41° and 173.90°). The differences in angles between Au-P-Ligand in both phosphines were observed, where the values of angles were respectively: 109.48° (proline derivative), 111.69° (Ph), 114.24° (Ph) for Au bridge with an angle between N-Au-P 173.90° and 110.20° (Ph), 112.78° (Ph), 116.56° (proline derivative) for Au bridge with an angle between N-Au-P 177.41°. These differences can explain two chemical shifts on the ^{31}P NMR.



196 **197**

Reagents: i) Me_2SAuCl, Ag_2CO_3, CH_2Cl_2, RT, 94%

Scheme 101

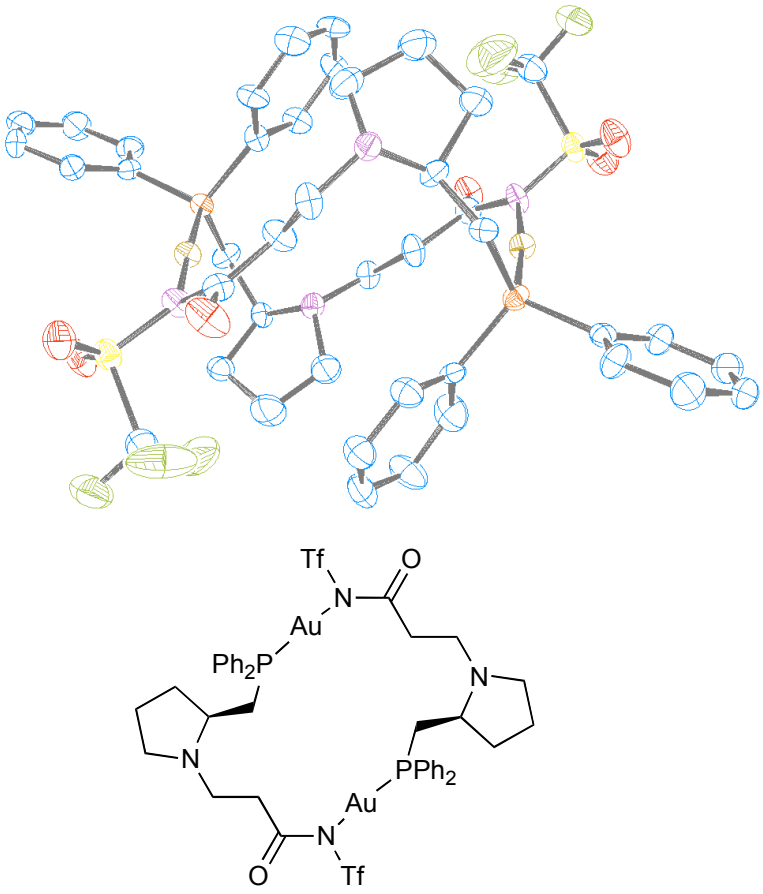
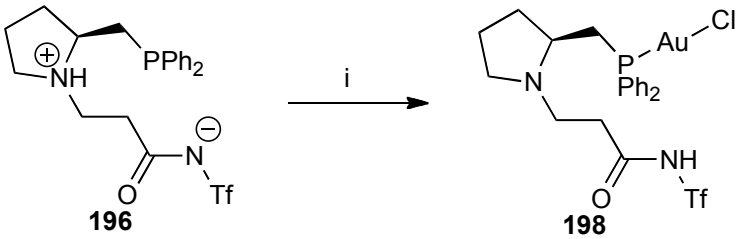


Figure 20

2.4.2.4.6 Synthesis of Gold(I) Complex with Bistriflic Imide

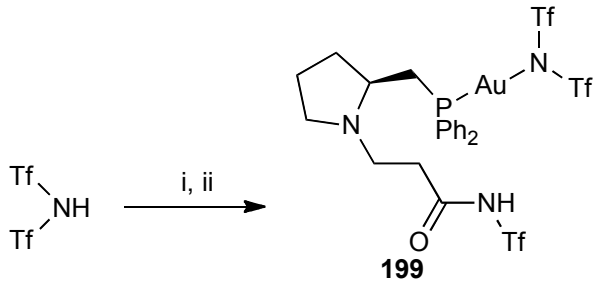
It was decided to synthesise the chiral gold bistriflic amide using compound **198** to compare reactivity and enantiomeric excess. The first step involved the preparation of chiral gold(I) phosphine chloride **198** (Scheme 102) in dichloromethane in the presence of dimethylsulfide gold chloride in 94% yield. The ^{31}P NMR showed a singlet at 26.38 ppm.



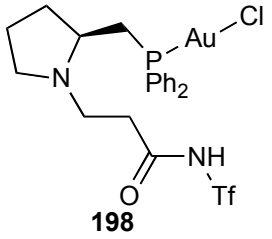
Reagents: i) Me_2SAuCl, CH_2Cl_2, R.T., 94%.

Scheme 102

In the second step, bistriflic imide was premixed with silver carbonate and after 5 minutes, gold(I) phosphine chloride **198** was added (Scheme 103). The desired product **199** was obtained in 80% yield. Surprisingly, ^{31}P NMR showed a singlet at 26.78 ppm, which is very similar to that of chiral gold(I) phosphine chloride **198**, however ^{19}F NMR showed two picks at -76.56 and -78.68 corresponding to two environmentally different triflic group. (The DOSY NMR of the product **199** and starting marerial **198** confirmed obtained result and the data is presented in Chapter 2.3.2.5.1). Compound appeared to be air stable however in chloroform colour of solution turned to red after a few hours what suggest decomposition of gold compound.



Reagents: i) Ag_2CO_3, CH_2Cl_2, RT,ii) **198**, 80%.



Scheme 103

2.4.2.4.7 Chain expansion

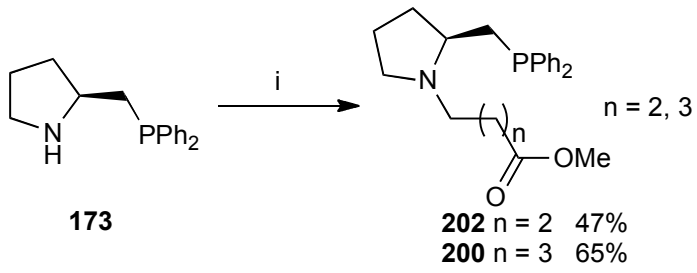
The computational experiments showed that the minimum ring size should be 9 membered,[110] however attempt to prepare the bidentate gold(I) complex with 9 membered ring failed and the dimer was formed.

It was decided to investigate the correlation between dimer/monomer chain size of the spacer in the pincer ligand. Incremental expansion of the chain could be achieved by utilising alkylating agents of suitable length.

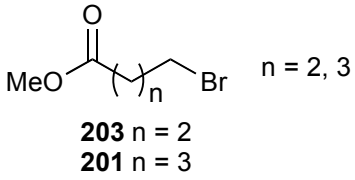
2.4.2.4.7.1 Synthesis of N-substituted (L)-2-((diphenylphosphino)methyl)pyrrolidines

In the previous synthesis of the bidentate gold(I) complex methyl 3-bromopropionate **191 or** was used, which contains the chain with two CH_2 elements. It was decided to attempt synthesis of the (*L*)-2-((diphenylphosphino)methyl)pyrrolidine with 3 and 4 CH_2 in the chain.

(*L*)-2-((diphenylphosphino)methyl)pyrrolidine with 4-carbon chain **200** was obtained by *N*-alkylation with methyl 5-bromopentanoate **201**, in the presence of triethylamine in dichloromethane in 65% yield (Scheme 104). The (*L*)-2-((diphenylphosphino)methyl)pyrrolidine with 3 CH_2-membered chain **202** was obtained with methyl 4-bromobutanoate **203** according the same procedure (Scheme 104). The methyl 4-bromobutanoate **203** can be prepared from γ-butyrolactone in methanol with gaseous hydrogen bromide according Franke's procedure.[163]



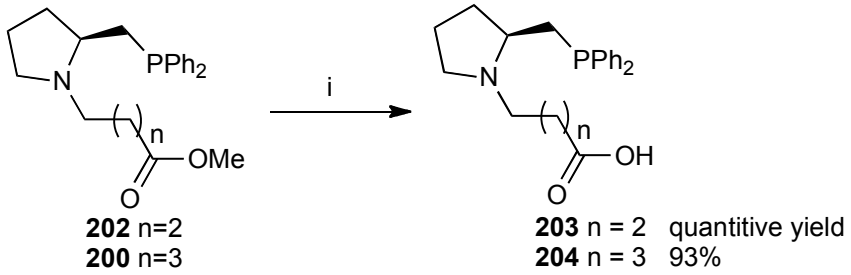
Reagents: i) **201** or **203**, Et_3N, CH_2Cl_2, 30 °C.



Scheme 104

2.4.2.4.7.2 Synthesis of (L)-3-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoic acid xx and (L)-3-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)butanoic acid

The next step was the preparation of the acid. This transformation was performed by saponification as used in the synthesis of (*L*)-3-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)propanoic acid **195** (Scheme 99). The compound **203** and **204** were obtained from compound **202** and **200** in quantitative yield and 93% yield respectively (Scheme 105).

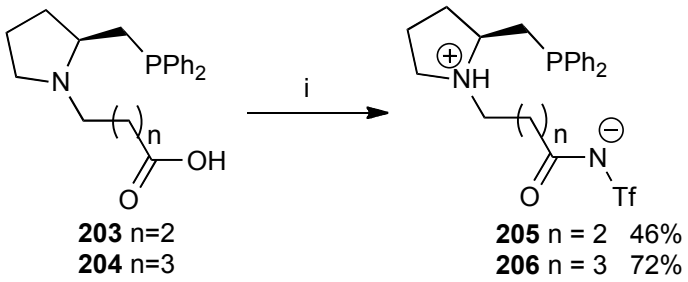


Reagents: i) 1 M NaOH aq., MeOH, R.T.

Scheme 105

2.4.2.4.7.3 Synthesis of (3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)pentanoyl)((trifluoromethyl)sulfonyl)amide and (3-((2S)-2-((diphenylphosphino) methyl)pyrrolidin-1-ium-1-yl)butanoyl)((trifluoromethyl)sulfonyl)amide

The amidation step was attempted using triflic amine **150** with corresponding acid **203** and **204** (Scheme 106) according Ostaszewski's procedure used successfully in the synthesis of the second generation gold(I) compound.[96] The products **205** and **206** were obtained in 46% and 72% yield (Scheme 106).



Reagents: i) **150**, HOBt·H_2O, EDC, CH_2Cl_2, 0 ºC - R.T.

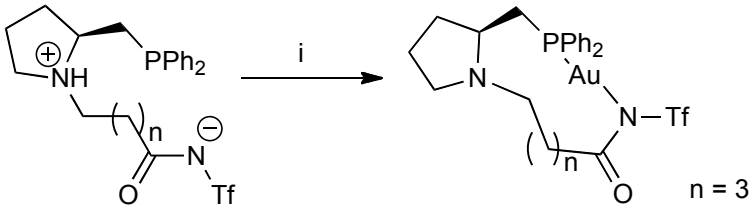
Scheme 106

2.4.2.4.7.4 Synthesis of Third Generation Gold(I) Compounds

The synthesis of gold(I) complexes were approached using condition used previous for the synthesis of the gold(I) complex with triflic amide **197** (Scheme 101).

The chemical shift of C=O for gold(I) compound with 4-carbon chain **207** (Scheme 107) shifted from 181.0 ppm to 178.8 ppm. The ^{31}P NMR showed a singlet at 16.51 ppm (Figure 21, Spectrum no.3) whilst the dimer **197** showed two singlets at 21.92 (s), 20.81 (s) (Figure 21, Spectrum no.1) (The assumption of dimer structure based on X-ray and high-resolution mass spectroscopy). The obtained ^{31}P NMR result suggest that the synthesised compound with 4-carbon chain in solution is monomer bidentate gold(I)

complex **207** (Scheme 107). However the X-ray diffraction measurement revealed that the compound **207** (Figure 22) is a dimer in the crystal submitted. The high-resolution mass spectroscopy showed mass of dimer and monomer.



206 **207**

Reagents: i) Me_2SAuCl, Ag_2CO_3, CH_2Cl_2, R.T., quantitive yield.

Scheme 107

The reaction with triflic amide **205** (Scheme 108) was performed under the same conditions as the reaction described above, however the obtained results were inconclusive. The high-resolution mass spectroscopy showed both the mass of dimer and the mass of the monomer. ^{31}P NMR showed three peaks at 23.06 (s), 21.55 (br, s), 19.68 (s) ppm (Figure 21, Spectrum no.2). One of the interpretations of this result could be a equilibrium between dimer **209** and **208** monomer products (Scheme 108) (two peaks for dimer and one for monomer).

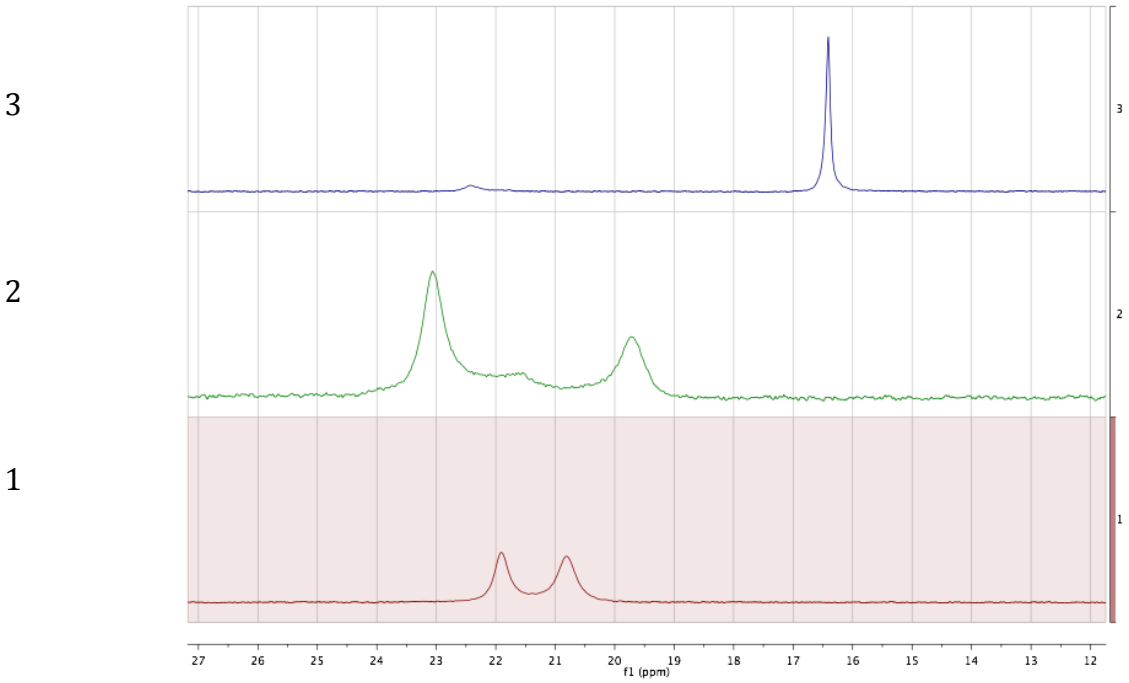
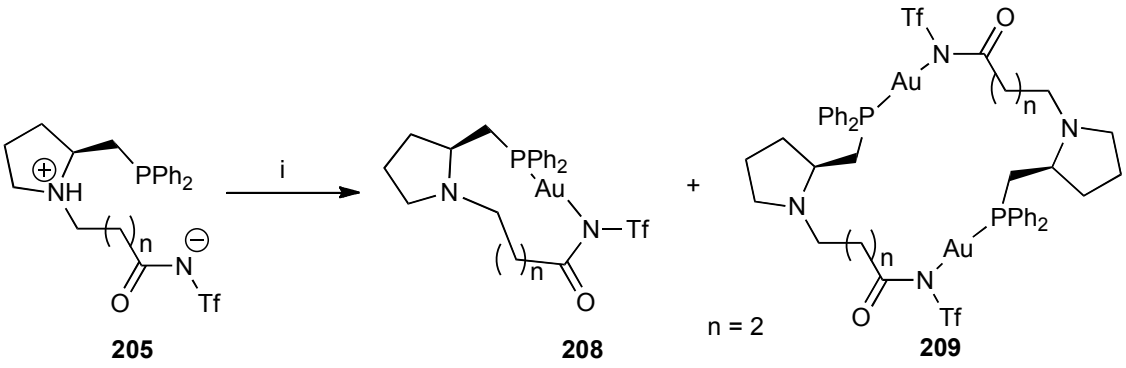


Figure 21



Reagents: i) Me_2SAuCl, Ag_2CO_3, CH_2Cl_2, R.T.

Scheme 108

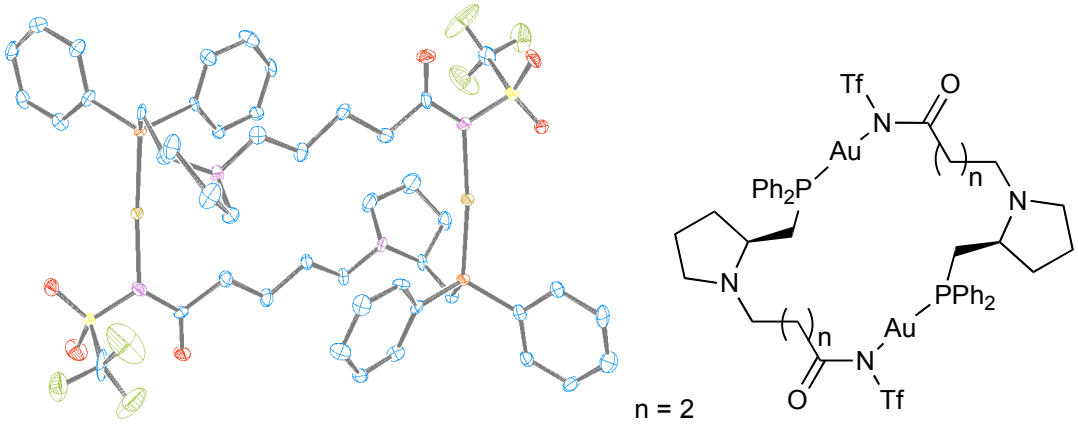


Figure 22

2.4.2.5 Investigation of the Aggregation State of the Catalysts in the Solution

The X-ray diffraction measurement of the third generation of the two of the gold compounds revealed the dimers in solid state. However, the question of whether the dimers might be stable in solution or the conversion into monomers would be observed. Three different methods were chosen to investigate the aggregation state of the gold(I) compounds: Diffusion-Ordered Spectroscopy, Freezing Point Depression and The Osmometric Method for Determining Molecular Weight (The equilibrium can be achieved after a few days, however unfortunately black film on the surface of the apparatus was observed which was an indication of the slow decomposition. The method appeared to be unsuitable for the investigation). The results of investigation are presented in chapter 2.4.2.5.1 and 2.4.2.5.2.

2.4.2.5.1 Diffusion-Ordered Specroscopy (DOSY)

Diffusion-ordered spectroscopy (DOSY) is a two-dimensional NMR experiment (one dimension accounts for conventional chemical shifts and the other for the diffusion) based upon the self-diffusion behaviour of individual molecules. The DOSY NMR has the potential to be a cheap and easy alternative to LC-NMR because it allows a precise analysis of a mixture without any prior separation of the compounds. The signal of each component decays with different diffusion rates as the gradient strength increases, constructing a bilinear NMR data set of a mixture. The diffusion coefficient (*D)* depends on properties of individual molecule such as size, shape, charge and surrounding environment (solution, temperature, aggregation state such as monomer, dimer, trimer, etc.).[164] This relationship can be defined by the Stock-Einstein equation[165] where the diffusion coefficient (*D*) is described by:

$$D = (k_B T) / (6\pi\eta r_H)$$

where:

k_B is Boltzmann's constant [JK^{-1}],

T is the absolute temperature [K],

η is viscosity [Pa•s],

r_H is the radius of the spherical particle [m].

Three experiments were prepared with gold compounds **197**, **208**/**209** and **207**. Deuterated chloroform with η = 0.542 x 10^{-3} Pa•s was chosen as an appropriate solvent for the experiments. A flow of solvent, which is related to temperature and viscosity, is generated through the sample caused by convection currents, and hence different rates of diffusion of the analyte would be observed, leading to poor quality data. To circumvent this, the experiments were established at 298 K in a 3 mm NMR tube. The results are shown in Table 23.

Table 23

Entry	Gold compound	Diffusion coefficient (*D*) [m^2 s^{-1}]	Radius (r_H) [Å]
1	2xCH_2 chain	3.2 x 10^{-10}	12.6
2	3xCH_2 chain	3.7 x 10^{-10}	10.9
3	4xCH_2 chain	4.4 x 10^{-10}	9.0

The results suggest that in solution compound **197** is a dimer with hydrodynamic radius r_H 12.6 Å (Entry 1). This result was confirmed by DOSY NMR of the starting material **196** for dimer where hydrodynamic radius was r_H 4.9 Å with diffusion coefficient D = 8.2 x 10^{-10} m^2s^{-1}. The hydrodynamic radius of starting material is more a twice smaller then hydrodynamic radius of gold compound. The gold chloride **198** (Chapter 2.4.2.4.6) gave a hydrodynamic radius r_H 6.2 Å (D = 6.5 x 10^{-10} m^2s^{-1}), which is 1.3 Å larger (26% larger) then the starting material **196** for dimer. The gold compound **199** with bistriflic amide ligand (Chapter 2.3.2.4.6) is slightly larger (0.5 Å, 8% larger) than gold chloride **198** (Chapter 2.4.2.4.6) with a hydrodynamic radius of r_H 6.7 Å (D = 6 x 10^{-10} m^2s^{-1}). These results confirmed our earlier assumption based on ^{31}P NMR, high–resolution mass spectroscopy and X-ray diffraction. Compound **207** with 4-carbon chain (Entry 3) is a monomer in solution with smaller hydrodynamic radius r_H 9 Å then compound **197** (Entry 1). This result was confirm by comparison to starting material for compound **206** with 4-carbon chain which gave hydrodynamic radius r_H 6 Å with D = 6.6 x 10^{-10} m^2s^{-1}. The Entry 2 showed that value of the hydrodynamic radius r_H for gold compound with 3-carbon chain is 10.9 Å between 12.6 and 9.0 Å. If the gold compound is a dimer the value should be larger then 12.6 Å (Entry 1, 2-carbon chain), however when the gold compound is a monomer the value should be smaller then 9.0 Å (Entry 3, 4-carbon chain). These results suggest that the equilibrium between the dimer and the monomer exist in solution on the time scale of the experiment (100 ms).

2.4.2.5.2 The Cryoscopic Method - Freezing Point Depression

Freezing point depression is a phenomenon that takes place when the freezing point of a solvent, is lowered (depressed) by the addition of another compound or a solute. When the solution is treated as an ideal solution, the freezing point depression depends only on solute concentration (m = molality) that can be easy linear estimated to the cryoscopic constant K_f [°C kg/mol] (Eq.1). Freezing point depression ΔT_f [ºC] can be used to evaluate the number of the solute particles (i = Van't Hoff factor), which can be considered as concentration. This is only effective in diluted solution.

$$\Delta T_f = K_f \cdot m \cdot i \qquad (1)$$

Freezing point depression is another technique that was chosen to examine and confirm aggregation state of gold compounds **197** (2-carbon chain) and **207** (4-carbon chain). The first step was to find an adequate solvent that: can dissolve gold compounds and has a freezing point, which is not too low and with high cryoscopic constant. 1,2-Dibromoethane was found as the best solvent with cryoscopic constant K_f= 12.5 [ºC/(mol kg^{-1})].[166]

88 mg of gold compound **207** (4-carbon chain) was taken and dissolved in 3.6890 g of 1,2-dibromoethane. Calculations using Eq.1 revealed that the theoretical freezing point depression ΔT_f for the dimer is 0.214 ºC and for monomer 0.428 ºC respectively. The experiment gave result 0.433 ºC which corresponding to the monomer (Figure 23).

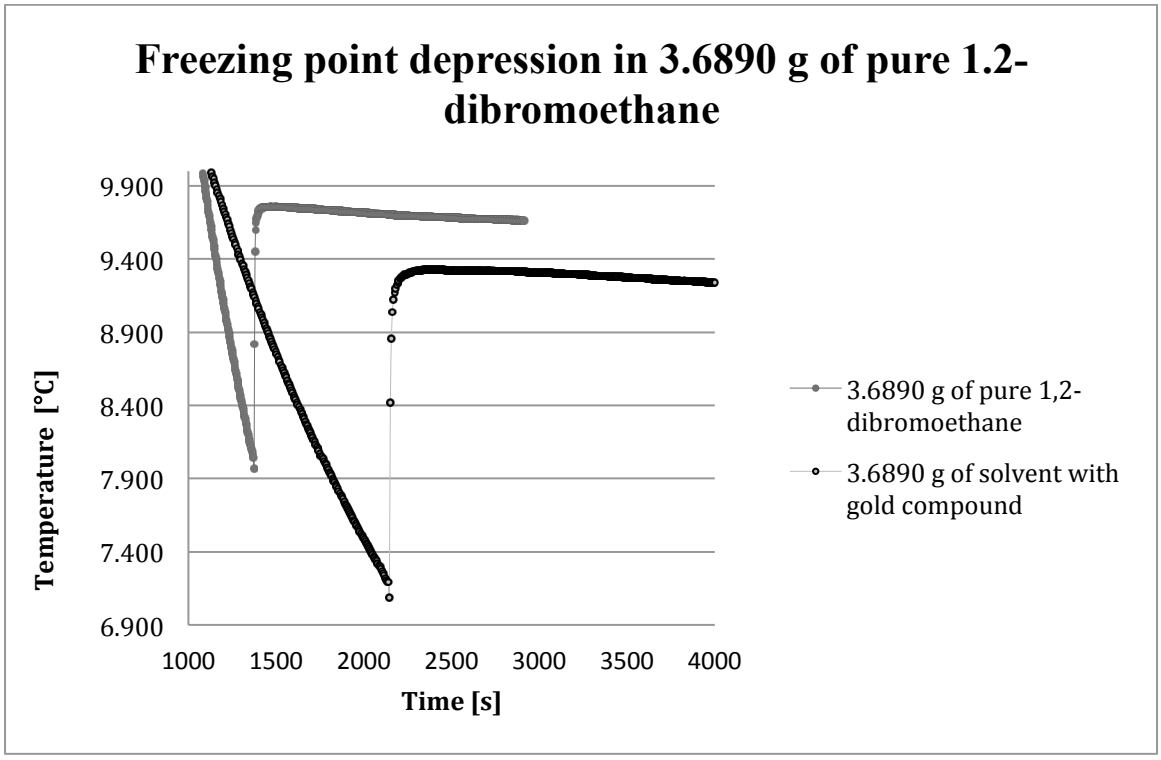


Figure 23

Sample of 58.5 mg of gold compound **197** (2-carbon chain) was taken and dissolved in 3.906 g of 1,2-dibromoethane. Basic calculations revealed that the theoretical

freezing point depression ΔT_f for the dimer is 0.138 ºC and for monomer 0.275 ºC respectively. The experiment gave result 0.133 ºC which corresponding to the dimer (Figure 24).

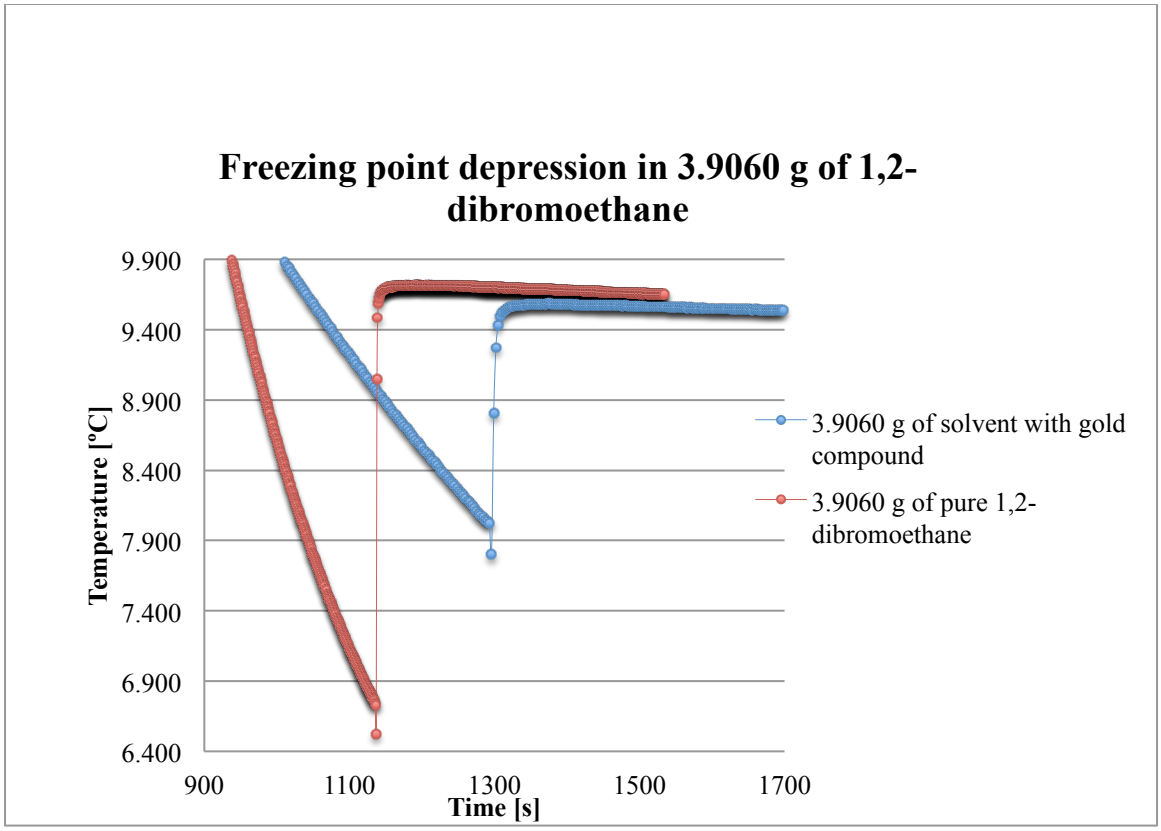


Figure 24

The experiments confirmed DOSY NMR results that in solution gold compound **207** is a monomer and gold compound **197** stayed dimer.

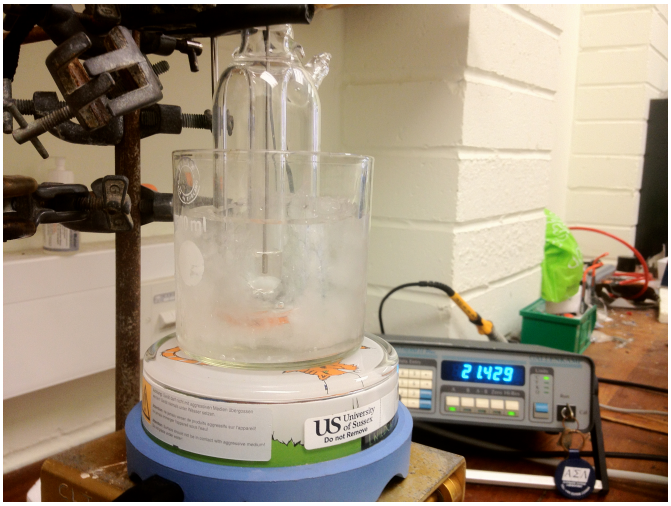


Figure 25

2.4.2.5.3 Summary of the Investigation of the Aggregation State

The summary of results of the investigation of the aggregation state is presented in Table 24. The investigation showed that the gold(I) compound **197** (2-carbon chain) in solution stayed as a dimer when the compound **207** (4-carbon chain) is a monomer in solution. The results of the gold(I) compound with 3-carbon chain suggest that the equilibrium between the dimer and the monomer exist in solution. The attempt of the crystallisation of the gold(I) compound with 3-carbon chain gave crystals unsuitable for X-Ray diffraction.

Table 24

	2-carbon chain (**197**)	3-carbon chain (**208**/**209**)	4-carbon chain (**207**)
^{31}P NMR (solution in $CDCl_3$, ε_r = 4.8 (293 K))	21.92 (s), 20.81 (s) ppm	23.06 (s), 21.55 (br, s), 19.68 (s) ppm	16.51 (s) ppm
High–resolution mass spectroscopy (solution in MeOH, ε_r = 33.95 (293.15 K))	**Dimer**	**Monomer/Dimer**	**Monomer/Dimer**
X-Ray (solid state)	**Dimer** Max radius 18.804 Å Min radius 8.421 Å	**-**	**Dimer** Max radius 20.255 Å Min radius 7.602 Å
DOSY (solution in $CDCl_3$, ε_r = 4.8 (293 K))	**Dimer** (r_H = 12.6 Å)	**Equilibrium between Dimer and Monomer** (r_H = 10.9 Å)	**Monomer** (r_H = 9 Å)
Freezing point depression (solution in 1,2-dibromoethane, ε_r = 10.5 (293.15 K))	**Dimer** (Expected: ΔT_f for dimer 0.138 ºC and for monomer 0.275 ºC Obtained: 0.133 ºC)	**-**	**Monomer** (Expected: ΔT_f for dimer 0.214 ºC and for monomer 0.428 ºC Obtained: 0.433 ºC)

ε_r is dielectric constant

2.4.2.6 Third Generation Gold(I) Complexes as a Catalyst for the Conia-ene Reaction

To verify the feasibility of Conia-ene transformation, a series of experiments (Table 25, Figure 26) was examined for the transformation of *β*-ketoester **16** to cyclopentane **17** (Scheme 109).

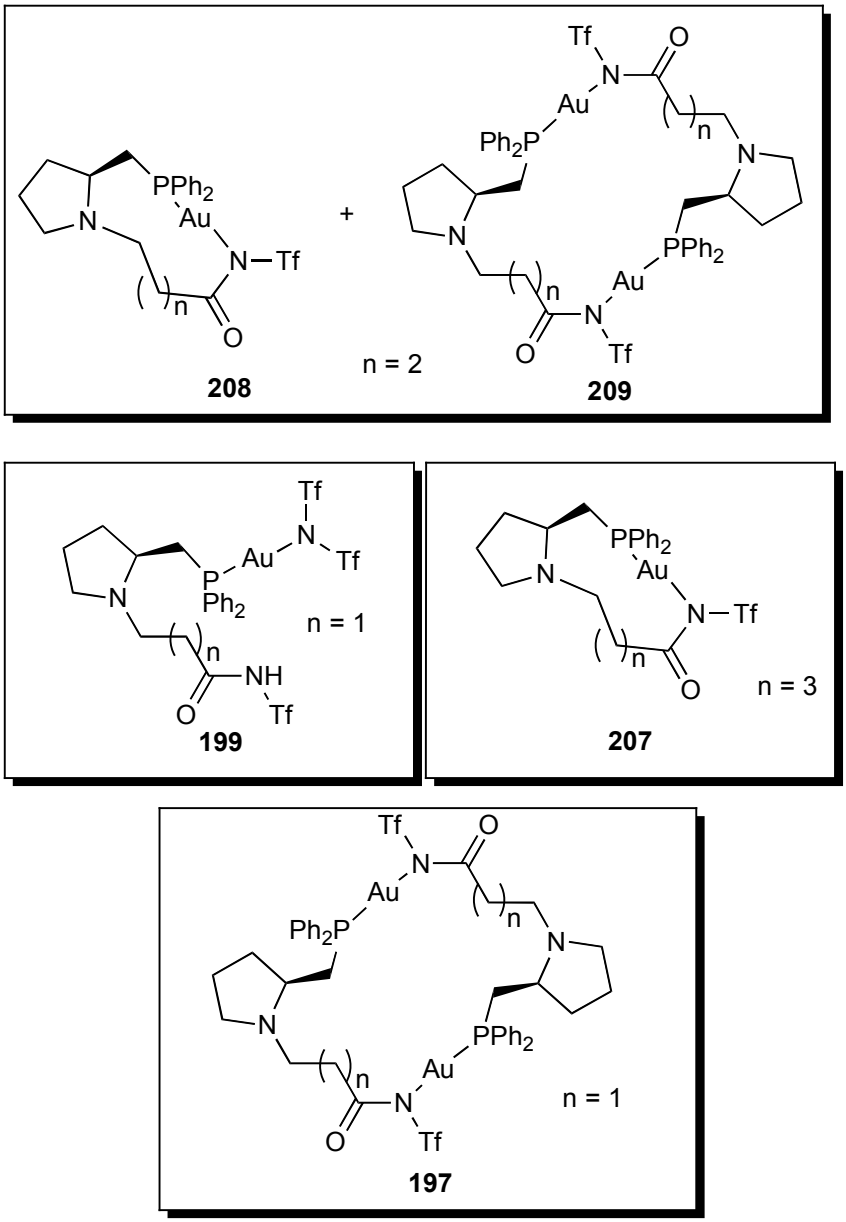
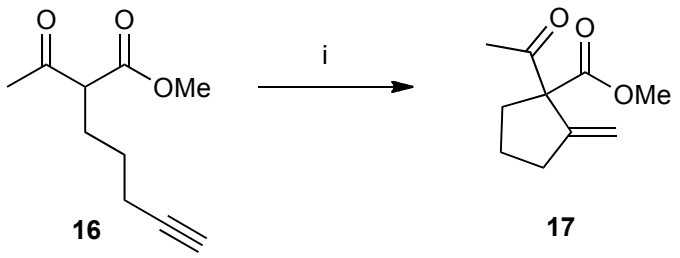


Figure 26



16 **17**

Reagents: i) see Table below

Scheme 109

Table 25

Entry	Cat.	Mol%	Solvent	Time	T [C°]	Yield [%]	$[\alpha]_D$[a]
1	**199**	1+1[b]	DCM	2 days	RT	73	-3.2
2	**199**	2	DCM	2 days	RT	65	-3.0
3	**199**	1	DCE	24 h	50	58	-1.2
4	**-**	-	DCE	24 h	50	<8	-
5	**197**	5	DCM	5 days	RT	33	2.4
6	**197**	5	DCE	14 h	70	75	3.2
7	**-**	-	DCE	14 h	70	13	0
8	**208/209**	5[c]	DCM	5 days	RT	Trace	-
9	**207**	5	DCM	5 days	RT	Trace	-

(a) The concentration of product was 10 mg in 1 mL of dichloromethane; (b) After 1 day another 1mol% was added; (c) The assumption was taken that only monomer was in the mixture of the monomer and dimer.

The substrate **16** underwent *5-endo-dig* cycloisomerisation with 2 mol% of the gold complex with bistriflic counterion (**199**) (Entries 1 and 2) in good yield. Increasing the temperature to 50 °C yielded 58% of product after 24 h, however with lower $[\alpha]_D$ and visible decomposition of catalyst (black film on surface of the round bottom flask) (Entry 3). To eliminate the possibility of a thermal cyclisation, which could adversely affect the result, the reaction was performed at 50 °C without catalyst (Entry 4). The mixture **208**/**209** (Entry 8) and bidentate gold complex **207** (Entry 9) gave only a trace of desired product, whilst dimer **197** gave *β*-ketoester **17** in 33% yield and, surprisingly, opposite

$[\alpha]_D$ compared to gold complex **199**. Further investigation revealed that the dimer can convert ketoester **16** into **17** in 75% yield in 1,2-dichloroethane at 70 °C, with larger $[\alpha]_D$ over 14 h, with apparent complete consumption of ketoester **16** (Entry 6). To eliminate the possibility of a thermal cyclisation, which could affect the result, the reaction was performed at 70 °C without catalyst (Entry 7).

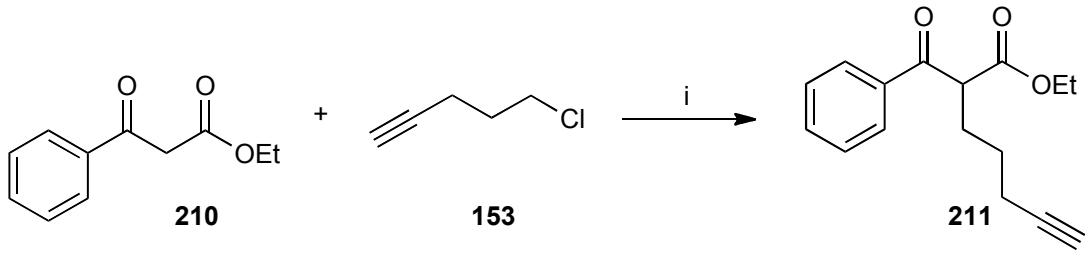
To exclude the possibility that the reaction in Scheme 109 (page 114) could be catalysed by ligand **196** by asymmetric organocatalysis[167-170] and examine the possibility of the Conia-ene with the gold/chiral auxiliary system, a series of experiments were performed (Table 26). None of the desired product was obtained, showing that neither ligand alone nor the gold/chiral auxiliary system worked.

Table 26

Entry	Cat. [mol%]	Ligand [mol%]	Solvent	T[°C]	Time	Result
1	-	**196** [5]	DCM	RT	3 days	/[a]
2	-	**196** [5]	DCE	50	4 days	/[a]
3	$Ph_3PAuNTf_2$ [1]	(*L*)-proline [20]	DCM	RT	5 days	/[a]
4	$Ph_3PAuNTf_2$ [1]	(*L*)-proline [20]	MeCN	70	5 days	/[a]
5	$Ph_3PAuNTf_2$ [1]	(*L*)-proline[100]	DCM	RT	5 days	/[a]

(a) Starting material recovered.

It was decided to examine an enolate alkylation with a more demanding compound. **211** was chosen due to stabilisation of enolate by mesomeric effect. The starting material was prepared according to Fournet's procedure with 5-chloropent-1-yne **153** and ethyl 2-benzoylhept-6-ynoate **210** (Scheme 110).

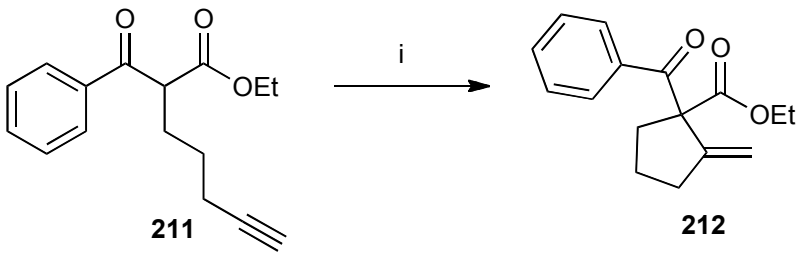


210 **153** **211**

Reagents: i) KI (0.5 eq.), NaH (1.1 eq.), THF/CH_2Cl_2, 24h, reflux, 83%.

Scheme 110

The series of experiments (Table 27) with newly synthesised gold(I) complexes (Figure 26, p. 113) was attempted. *β*-ketoester **211** (Scheme 111) underwent less then 10% conversion to product **212** with gold-complex **199** after 7 days at room temperature (Entry 3). When the less reactive dimer **197** was used only a trace of compound was obtained (Entry 2). However when the reaction was performed at 70 °C with dimer **197** the yield reached 91%, which suggests that an activation energy of the Au-catalyst reaction (Entry 1) as the reaction does not proceed without catalyst at that temperature (Entry 8). The yields with a mixture of monomer and dimer **208**/**209** (Entry 5) and with monomer **207** alone (Entry 7) were similar at 70 °C. All of the complexes are based on (*L*)-prolinol, however the dimer **197** gave a positive rotation of the product **212** ($[\alpha]_D$ = 8.4) (Entry 1), whilst the monomer **207** showed a negative rotation of the product **212** ($[\alpha]_D$ = -3.4) (Entry 7). The poor enantiomeric excess could be a consequence of the linear geometry of gold(I) complexes[104] or possible change of the structure or conformation of the catalyst during the reaction. In Entry 5 with mixture of dimer and monomer (**208**/**209**) the measured $[\alpha]_D$ was zero.



211 **212**

Reagents: i) see Table below

Scheme 111

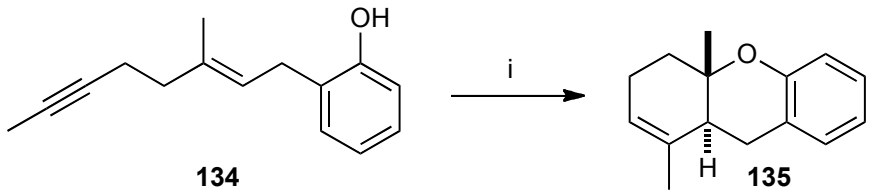
Table 27

Entry	Cat.	Mol%	Solvent	Time	T [C°]	Yield [%]	$[\alpha]_D$[a]
1	**197**	5	DCE	5 days	70	91	8.4
2	**197**	5	DCM	7 days	RT	Trace	-
3	**199**	2	DCM	7 days	RT	<10	-
4	**208/209**	5[b]	DCM	7 days	RT	Trace	-
5	**208/209**	5[b]	DCE	7 days	70	52	0.0
6	**207**	5	DCM	7 days	RT	Trace	-
7	**207**	5	DCE	7 days	70	51	-3.4
8	-	-	DCE	2 days	80	-	-

(a) The concentration of product was 10 mg in 1 mL of dichloromethane; (b) The assumption was taken that monomer was solely present in the mixture of the monomer and dimer.

2.4.2.7 Third Generation Gold(I) Complexes as a Catalyst in Cycloisomerisation Reaction

The *6-endo-dig* phenoxycyclisation reaction of 1,5-enyne (**134**) substrate was attempted in the presence of gold(I) complexes **197**, **199** and mixture **208/209** (Figure 26, p. 113) at room temperature. The use of mixture **208/209** led to only traces of product **135**. The complex **199** led to clean formation of product **135** in 67% yield but with an $[\alpha]_D$ is only 1.8 (Entry 2). The use of dimer complex **197** gave a slightly lower yield but better $[\alpha]_D$ (Entry 1).



Reagents: i) see Table below

Scheme 112

Table 30

Entry	Cat. [mol%]	Solvent	Time	T [C°]	Yield [%]	$[\alpha]_D$[a]
1	**4** [5]	DCM	7 days	RT	55	4.0
2	**3** [2]	DCM	2 days	RT	67	1.8
3	**5** [5][b]	DCM	7 days	RT	Trace	-

(a) The concentration of product was 10 mg in 1 mL of dichloromethane; (b) The assumption was taken that only monomer was in the mixture of the monomer and dimer.

2.4.2.8 Conclusion

In conclusion, a new model for a series of chiral bidentate gold(I) catalyst was synthesised, which could be further developed. It was experimentally found that the optimal size is a 12-membered ring to allow having the correct linear geometry of P-Au-NTf. The modification of the triphenylphosphine ligand through exchanging one phenyl group for (*L*)-prolinyl group allow to synthesise bidentate the ligand which yielded the synthesis of third generation of gold(I) complexes. The triflic amide couterion appears to be efficient and should have many applications in gold catalysis in the future.

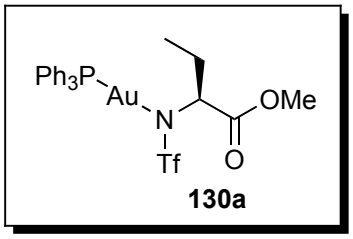
3. General Conclusion and Future Work

3.1 General Conclusion

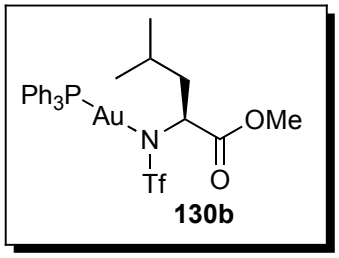
This manuscript presents the development of novel chiral gold(I) complexes and results obtained in the area of homogeneous gold catalysis.

During the investigation three generations of new gold(I) compounds were successfully synthetised (Figure 27) and investigated with *6-endo-dig* phenoxycyclisation reaction of 1,5-enyne and *5-exo-dig* cyclisation known as Conia-ene reaction though the activation of the triple bond.

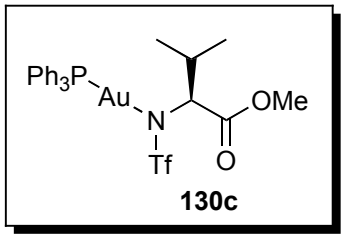
I generation of gold(I) compounds



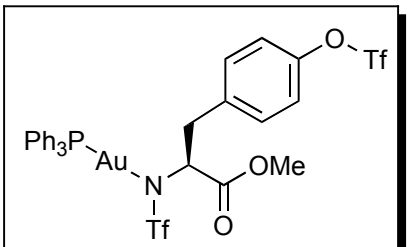
130a



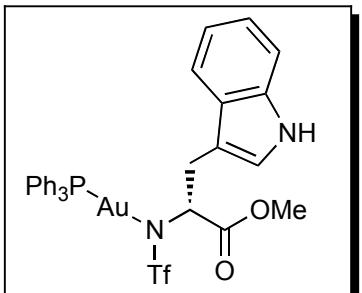
130b



130c

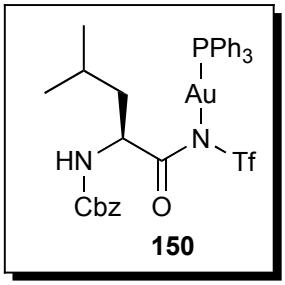


130d

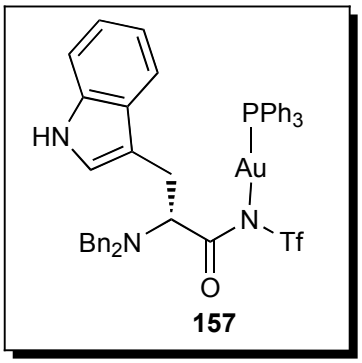


130e

II generation of gold(I) compounds



150



157

III generation of gold(I) compounds

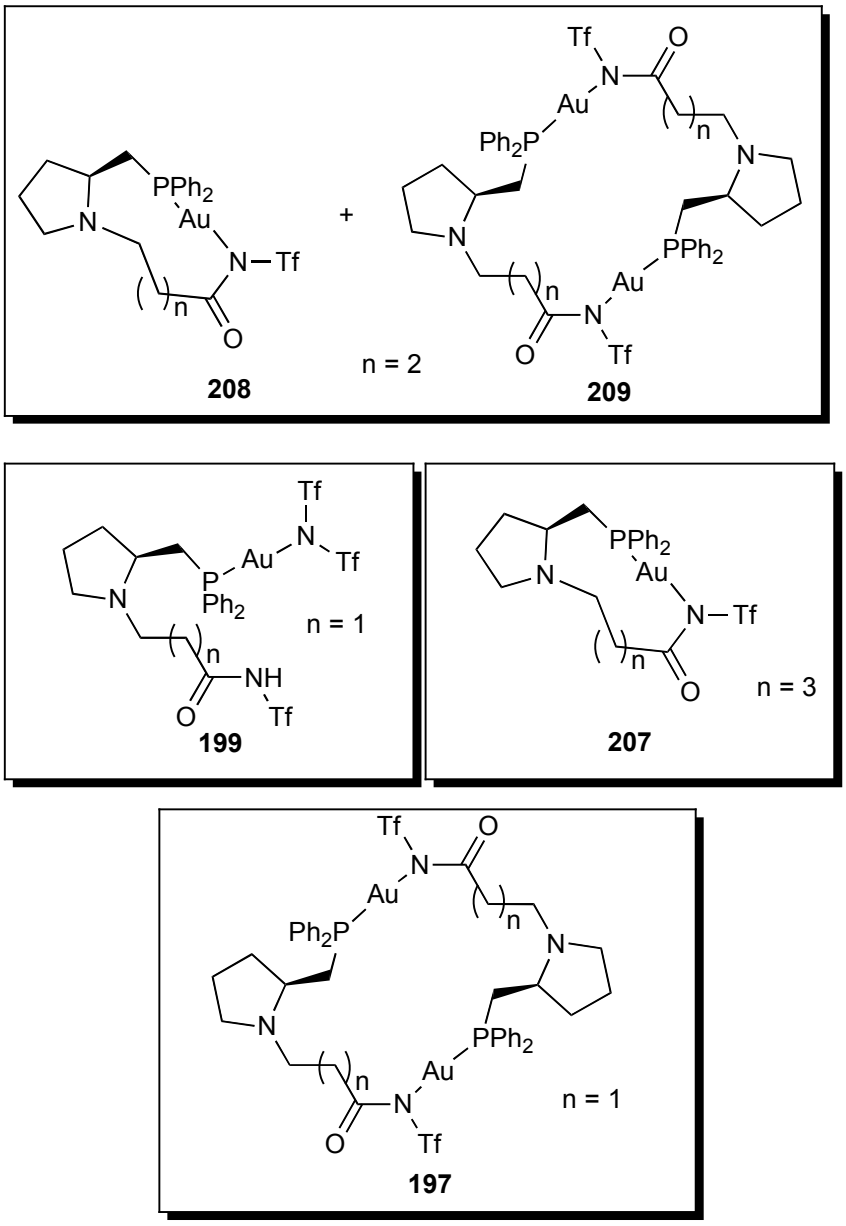


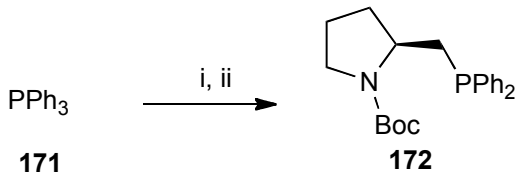
Figure 27

The synthetised gold(I) complexes proved to be air-stable, easy to synthesise, storable and handle in laboratory.

The new counterion developed during our investigation was based on a nitrogen ligand bearing two mixed withdrawing groups that proved essential to obtain good catalytic activity. One sulfonamide alone was not sufficient to render the X ligand labile for the generation of the active cationic gold species. This observation paved the ground

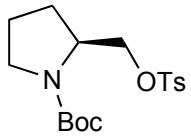
for the synthetise of bidentate precursors in our third generation of gold(I) complexes. Though the second and third generations of gold(I) complexes did show catalytic activity, the third generation successfully introduced chirality in the model reactions, albeit in very modest ratios (Figure 27, p. 120).

The modification of the Tomioka's procedure led to the preparation of chiral phosphines in good yields, avoiding the manipulation of the highly reactive diphenylphosphine which can readily oxidise when exposed to traces of oxygen. The ligands were obtained in a one pot procedure involving the lithiation of triphenylphosphine and subsequent substitution of a tosylated alcohol (Scheme 113).



171 **172**

Reagents: i) Li, THF, RT; ii) **170**, RT, 60%.



170

Scheme 113

The novel route to chiral phosphines based on (*L*)-prolinol involved the use of sulfamidates, which served two purposes: the protection of the secondary amine and the activation of the hydroxy group towards nucleophilic substitutions.

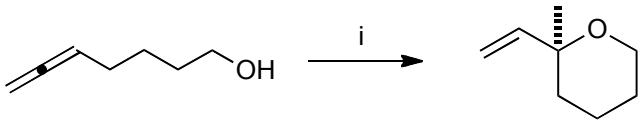
Finally some of the gold(I) compounds as well as precursors were crystallised using different methods and desired structures were confirmed by X-ray diffraction measurement.

The aggregation state of the third generation of bidentate gold(I) complexes was investigated in solution using two different methods: Diffusion-Ordered Spectroscopy, Freezing Point Depression. These methods proved the aggregation state of third generation of gold(I) complexes in solution. The investigation showed that the gold(I) compound **197** (2-carbon chain) in solution stayed as a dimer when the compound **207** (4-carbon chain) is a monomer in solution (dimer in solid state).

3.2 Future Work

With the molecules depicted in this manuscript a number of interesting extensions could be envisaged:

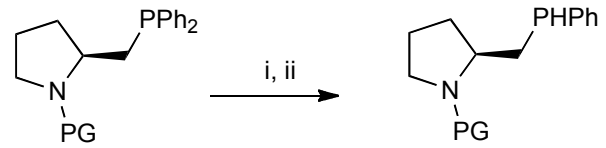
- The use of second generation gold(I) complexes with allenes as the starting material (Scheme 114). As seen in Chapter 1.4.1 page 36, allenes were successfully used during hydroalkoxylation,[67] hydroamination[66] and hydrocarboxylation[66,68,69] reactions with chiral counterions in gold catalysis. The change of hybridisation of the allene from sp^2 to sp^3 during a gold-catalysed addition is key to high e.e.s as the newly introduced chiral centre is generated very close to the chiral complex, unlike a Conia-ene cyclopentannulation (Chapter 1.4.2.2, p. 48) where any remote asymmetric control failed under gold catalysis. Good e.e.s were obtained under Pd-catalysis, presumably by reductive elimination to the cyclopentane whereby the newly generated chiral centre is directly attached to the chiral palladium complex.



Reagents: i) II[nd] generation gold(I) complex, solvent.

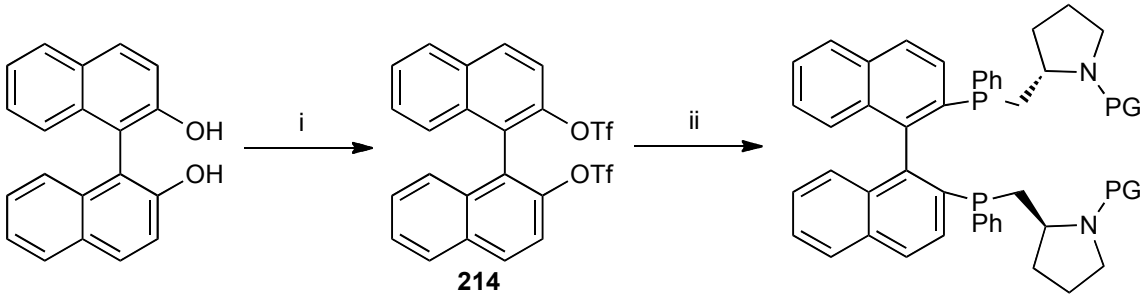
Scheme 114

- The introduction of chiral phosphine (**213**) to (*R*) or (*S*)-1,1'-bi-2-naphtol bis(trifluoromethanesulfonate) (**214**) (Scheme 115). This attempt can introduce chiral phosphine (**213**) in atropisomer (**214**) with restricted rotation about the aryl-aryl bond, and can potentially yield five centres of chirality (two of which can be obtained as a P-chiral centres) and steric hindrance. The methodology provided in this manuscript can lead to a novel class of bidentate gold(I) chiral catalysts.



213

Reagents: i) 2 eq. Li, THF, R.T.; ii) H_2O



214

Reagents: i) Tf_2O, pyridine; ii) **213**, 10% $NiCl_2$dppe, DMF, DABCO, 100 ^oC.

Scheme 115

4. Experimental

4.1 General Procedures

All reagents and solvents were used without further purification from commercially available sources unless otherwise stated.

Dry diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone under an atmosphere of nitrogen. Dichloromethane, toluene, triethylamine, and diisopropylamine were distilled from calcium hydride under atmosphere of nitrogen.

Under anhydrous conditions, all apparatus was flame-dried before either cooling in sealed dessicator containing silica gel, cooling under vacuum (0.3 mmHg) or under a continuous flow of nitrogen or argon.

Evaporation under reduced pressure was performed on a Büchi rotary evaporator, using house vacuum (30 mmHg). Reduced pressure was achieved by using a static oil pump (0.05 mmHg) unless otherwise stated.

4.2 Spectroscopy and Analysis

The IR spectra were recorded on spectrometer Perkin Elmer FT-IR Spectrum One equipped with a diamond top plate.

Mass spectra were obtained by using VG Autospec Magnetic Sector MS and Bruker Daltonic FT-ICR-MS Ape III instruments, using electron impact (EI) or fast atom bombardment (FAB).

The ^{1}H nuclear magnetic resonance spectra were recorded on a Varian 400 (400 MHz) or Varian 500 (500 MHz). Chemical shifts are reported in parts per million (ppm) relative to residual $CHCl_3$ (δ 7.26 ppm), H_2O (δ 4.80 ppm), DMSO (δ 2.50 ppm), CH_3OH (δ 4.87 ppm). The following abbreviations are used to describe the multiplicity of given signals: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, sept = septet, m = multiplet and br = broad. Coupling constants, *J*, are given wherever appropriate in Hertz.

The ^{13}C nuclear magnetic resonance spectra were recorded on a Varian 500 (126 MHz). Chemical shifts are reported in parts per million (ppm) relative to $CDCl_3$ (central line of triplet δ 77.00 ppm), DMSO (central line of septet δ 39.51 ppm), CD_3OD (δ 49.15

ppm). The following abbreviations are used to describe the multiplicity of given signals: C = quaternary, CH = methane, CH_2 = methylene, CH_3 =methyl. Coupling constants, *J*, are given wherever appropriate in Hertz.

The ^{31}P nuclear magnetic resonance spectra were recorded on a Varian 400 (162 MHz) referred to 85% phosphoric acid in water.

The ^{19}F nuclear magnetic resonance spectra were recorded on a Varian 400 (376 MHz).

The DOSY NMR spectra were recorded on a Varian 600 with the diffusion labeling period 100 ms.[171] The spectra were proceeded with DOSY Toolbox.[172]

The freezing point depression was measured at AutoTherm II Plus thermometer in high-resolution mode (DIN standard). The data was proceeded with Metter Toledo program. Platinum resistance thermometer (no. 515-131) probe was used with error:

0.001 °C for 10.048 °C

-0.004 °C for 5.041 °C

4.3 Chromatography

All reactions were monitored, where appropriate, by T.L.C. using Macherey-Nagel plates with a 0.2 mm layer of 60 F_{254} silica gel containing a fluorescent indicator. Visualization was achieved with U.V. light (254 mm) followed by an ethanolic solution of phosphomolibdic acid.

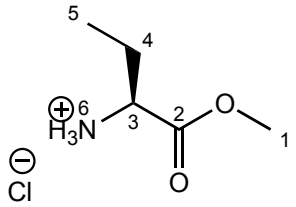
Flash column chromatography was carried out using Apollo Zeoprep 60 Hyd 35-70 micron silica gel.

Petroleum ether (PET) usually refers to the fraction distilled narrow alkene hydrocarbons distillate fraction from crude oil in the 40 to 60 °C ranges, unless otherwise stated, and was distilled prior to use.

4.4 Assignment of Data

All novel compounds are illustrated in full structural form with numbering of each individual carbon, independently of the IUPAC nomenclature. The ^{1}H and ^{13}C NMR data are assigned using the depicted numbering.

(2*S*)-1-methoxy-1-oxobutan-2-aminium chloride (132a)



Appearance: white solid **Yield:** quantitative

---

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.66 (3H, s, 6-H), 4.16 (1H, s, 3-H), 3.84 (3H, s, 1-H), 2.15 (2H, s, 4-H), 1.12 (3H, s, 5-H).

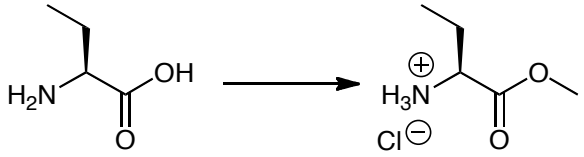
^{13}C NMR (126 MHz, $CDCl_3$) δ = 169.9 (2-C), 54.8 (3-CH), 53.9 (1-CH_3), 24.1 (4-CH_2), 9.9 (5-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 2874 (NH st), 1742 (C=O st), 1230 (CO-O st as), 1187 (C-O st as).

Acc. Mass (FAB): $C_5H_{12}NO_2$

Found: 118.0864 m/z *Err[ppm]: -1.62*

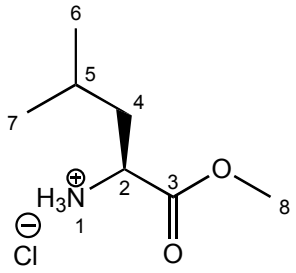
Calculated: 118.0863 m/z



Procedure

Thionyl chloride (1.385 g, 11.64 mmol, 0.85 mL) was added to a solution of (*L*)-2-amino-*n*-butynic acid (0.600 g, 5.81 mmol) in methanol (40 mL). The mixture was heated to reflux with vigorous agitation for 18 h. After cooling, the reaction mixture was concentrated under reduced pressure and the residual methanol traces were removed by azeotropic distillation with dichloromethane (10 mL) under reduced pressure to give the title compound as a white solid (0.894 g, quantitative).

(2*S*)-1-methoxy-4-methyl-1-oxopentan-2-aminium chloride (132b)



Appearance: white solid **Yield:** quantitative

---

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.81 (3H, s, 1-NH), 4.11 (1H, s, 2-H), 3.81 (3H, s, 8-H), 1.91 (3H, m, 4, 5-H), 0.99 (6H, d, *J*=4.3, 6, 7-H).

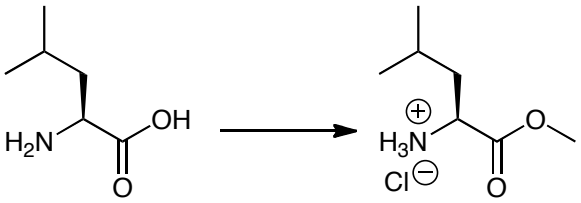
^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.1 (3-C), 53.1 (2-CH), 51.8 (8-CH_3), 39.5 (4-CH_2), 24.2 (5-CH), 22.3 (7-CH_3), 22.0 (6-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 2844 (N^+-H st), 1737 (C=O st), 1226 (CO-O st as), 1174 (C-O st as).

Acc. Mass (FAB): $C_7H_{16}NO_2$

Found: 146.1177 m/z *Err[ppm]: -1.19*

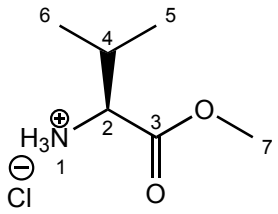
Calculated: 146.1177 m/z



Procedure

Thionyl chloride (2.722 g, 22.88 mmol, 1.67 mL) was added to the solution of (*L*)-leucine amino acid (1.500 g, 11.44 mmol) in methanol (76.27 mL). The mixture was heated to reflux with vigorous agitation for 24 h. After cooling, the reaction mixture was concentrated under reduced pressure and the residual methanol traces were removed by azeotropic distillation with dichloromethane (10 mL) under reduced pressure to give the title compound as a white solid (2.077 g, quantitative).

(2*S*)-1-methoxy-3-methyl-1-oxobutan-2-aminium chloride (132c)



Appearance: white solid **Yield:** quantitative

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.80 (3H, s, 1-NH), 3.97 (1H, d, *J*=3.1, 2-H), 3.81 (3H, s, 7-H), 2.46 (1H, d, *J*=3.9, 4-H), 1.14 (6H, dd, *J*=4.0, 6.5, 5, 6-H).

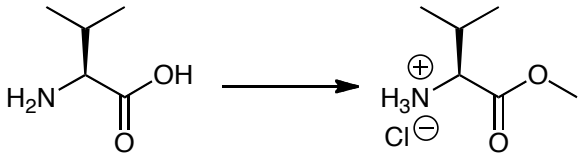
^{13}C NMR (126 MHz, $CDCl_3$) δ = 168.8 (3-C), 58.6 (2-CH), 52.9 (7-CH_3), 29.9 (4-CH), 18.4 (6-CH_3), 18.3 (5-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 2968, 2841 (N^+-H st), 1736 (C=O st), 1505 (CH_3 as) 1237 (CO-O st as), 1156 (C-O st as).

Acc. Mass (FAB): $C_6H_{14}NO_2$

Found: 132.1021 m/z *Err[ppm]: -1.53*

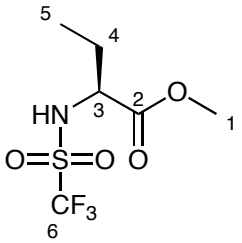
Calculated: 132.1019 m/z



Procedure

Thionyl chloride (25.60 mmol, 1.87 mL) was added dropwise to the solution of (*L*)-Valine amino acid (1.500 g, 12.80 mmol) in methanol (85 mL). The mixture was heated to reflux with vigorous agitation for 24 h. After cooling, the reaction mixture was concentrated under reduced pressure and the residual methanol traces were removed by azeotropic distillation with dichloromethane (10 mL) under reduced pressure to give the title compound as a white solid (2.149 g, quantitative).

(*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate (133a)



Appearance: yellow oil **Yield:** 85%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 5.77 (1H, br s, NH), 4.24 – 4.19 (1H, s, 3-H), 3.82 (3H, s, 1-H), 2.00 – 1.76 (2H, m, 4-H), 1.00 (3H, s, 5-H).

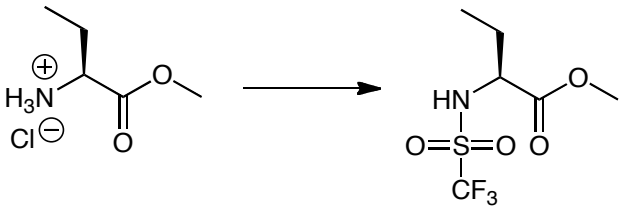
^{13}C NMR (126 MHz, $CDCl_3$ δ = 171.3 (2-C), 123.3 (6-CF), 120.8 (6-CF), 118.2 (6-CF), 115.7 (6-CF), 58.1 (3-CH), 53.0 (1-CH_3), 26.8 (4-CH_2), 9.0 (5-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 3271**,** 2980 (NH st), 1732 (C=O st), 1230 (CO-O st as), 1230 (C-O st as), 1185 (S-O st as), 1143 (S-O st sy).

$[\alpha]_D^{26}$=10.9 (*c*=1.0 in dichloromethane).

M.S. (EI) m/z

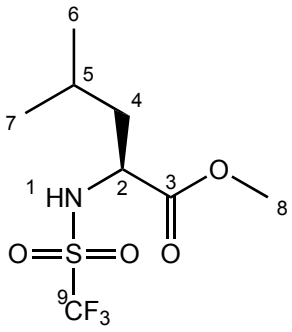
250 ($M^{+\cdot}$, 36%), 204 (10), 190 ($M^{+\cdot}$ - $C_2H_3O_2^{\cdot}$, 85%), 152 (38), 133 ($M^{+\cdot}$ – $C_5H_{10}NO_2^{\cdot}$, 6 %), 98 (37), 78 (12), 69 (67), 43 (49), 28 (65).



Procedure

A solution of triflic anhydride (1.603 g, 5.68 mmol) in dichloromethane (5.5 mL) was dripped into a solution of (2*S*)-1-methoxy-4-methyl-1-oxopentan-2-aminium chloride (0.873 g, 5.68 mmol) and triethylamine (1.150 g, 11.36 mmol) in dichloromethane (22 mL) at -78°C. The mixture was stirred for 24 h at room temperature. Water was added and the pH was adjusted to pH=5 using conc. hydrochloric acid. The aqueous layer was extracted with diethyl ether. The organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as an yellow oil (1.203 g, 85%).

Methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate (133b)



Appearance: yellow oil **Yield:** 77%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.22 (1H, dd, *J*=5.4, 9.0, 2-H), 3.79 (3H, s, 8-H), 1.84 – 1.75 (1H, m, 5-H), 1.70 – 1.57 (2H, m, 4-H), 0.97 (6H, dd, *J*=4.5, 6.1; 6, 7-H).

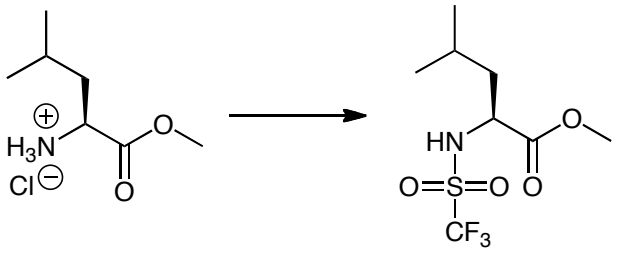
^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.9 (3-C), 120.7 (9-CF), 118.2 (9-CF), 55.7 (2-CH), 52.9 (8-CH_3), 42.5 (4-CH_2), 24.3 (5-CH), 22.6 (6-CH_3), 21.4 (7-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 3256 (NH st), 1733 (C=O st), 1227 (CO-O st), 1230 (S-O st as), 1143 (S-O st sy).

$[\alpha]_D^{25}$=-4.2 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_8H_{14}F_3NO_4SNa$
Found: 300.0491 m/z *Err[ppm]: -1.21*
Calculated: 300.0488 m/z

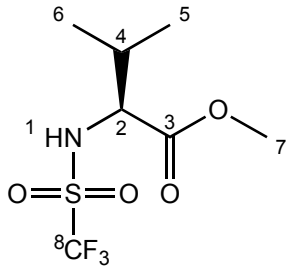
Rf (diethyl ether): 0.81 (green, PMA dip)



Procedure

A solution of triflic anhydride (3.183 g, 11.28 mmol) in dichloromethane (11.29 mL) was dripped into a solution of (2*S*)-1-methoxy-4-methyl-1-oxopentan-2-aminium chloride (2.049 g, 11.28 mmol) and triethylamine (3.426 g, 33.86 mmol) in dichloromethane (43 mL) at -78°C. The mixture was stirred for 24 h at room temperature. Water was added and the pH was adjusted to pH=5 using conc. hydrochloric acid. The aqueous layer was extracted with diethyl ether. The organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as an yellow oil (2.421 g, 77%).

Methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-valinate (133c)



Appearance: yellow oil **Yield:** 72%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.07 (1H, d, *J*=4.8, 2-H), 3.81 (3H, s, 7-H), 2.24 – 2.17 (1H, m, 4-H), 1.04 (3H, d, *J*=6.8, 6-H), 0.93 (3H, d, *J*=6.8, 5-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.9 (3-C), 120.8 (8-CF), 118.2 (8-CF), 62.4 (2-CH), 52.8 (7-CH_3), 31.6 (4-CH), 18.7 (6-CH_3), 17.0 (5-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 3150 (NH st), 1730 (C=O st), 1228 (CO-O st), 1182 (S-O st as), 1143 (S-O st sy).

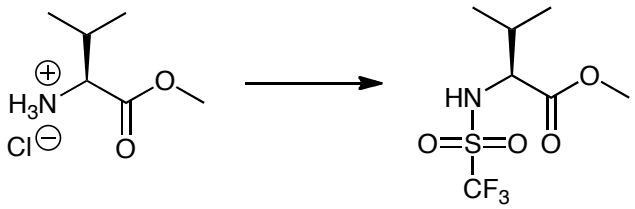
$[\alpha]_D^{26}$= N/A (*c*=1.0 in dichloromethane), the significant result was not obtained.

Acc. Mass (FAB): $C_7H_{12}F_3NO_4SNa$

Found: 286.0331 m/z *Err[ppm]: -0.26*

Calculated: 286.0337

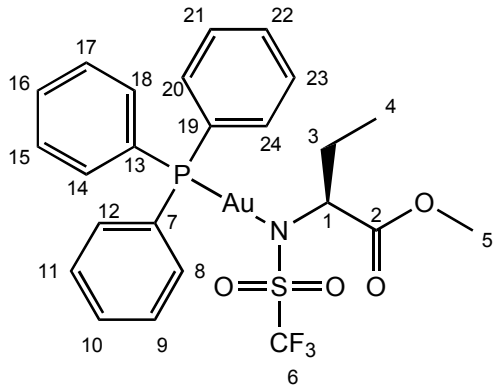
Rf (diethyl ether): 0.84 (green, PMA dip)



Procedure

A solution of triflic anhydride (3.581 g, 12.69 mmol) in dichloromethane (12.69 mL) was dripped into a solution of (2*S*)-1-methoxy-3-methyl-1-oxobutan-2-aminium chloride (2.128 g, 12.69 mmol) and triethylamine (3.854 g, 38.08 mmol) in dichloromethane (49 mL) at -78°C. The mixture was stirred for 24 h at room temperature. Water was added and the pH was adjusted to pH=5 using conc. hydrochloric acid. The aqueous layer was extracted with diethyl ether. The organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as an yellow oil (2.433 g, 72%).

Triphenylphosphine gold (*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate (130a)



Appearance: white solid **Yield:** 94%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.59 – 7.45 (15H, m, 7-24-H), 4.51 (1H, s, 1-H), 3.73 (3H, s, 5-H), 2.01 – 1.80 (2H, m, 3-H), 1.07 (3H, t, *J*=7.4, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.5 (2-C), 134.2 (Ar), 134.1 (Ar), 131.9 (d, *J*=2.4, Ar), 129.3 (Ar), 129.2 (Ar), 129.0 (Ar), 128.5 (Ar), 122.2 (6-CF), 119.7 (6-CF), 128.5 (Ar), 62,0 (1-CH), 51.9 (5-CH_3), 29.6 (3-CH_2), 10.3 (4-CH_3).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 31.57 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 3256 (ar CH st), 2170 (Ar comb), 1742 (C=O st), 1212 (CO-O st), 1174 (S-O st as), 1103 (S-O st sy).

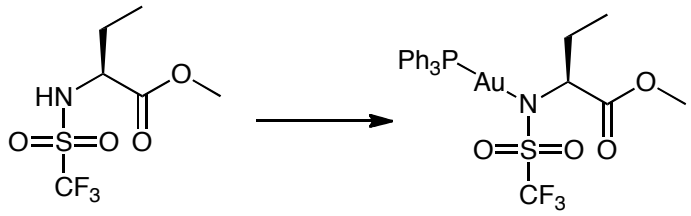
$[\alpha]_D^{27}$=−13.0 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{24}H_{24}AuF_3NO_4PSNa$

Found: 730.0730 m/z *Err[ppm]: -7.80*

Calculated: 730.0673 m/z

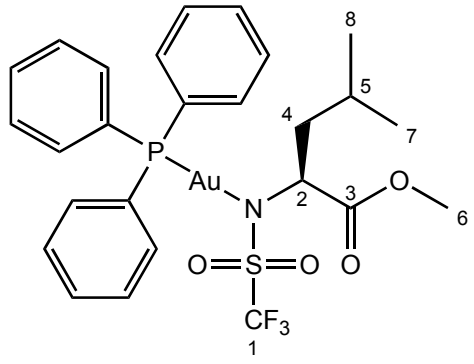
X-Ray: see appendix **130a** (The complex (0.402 g, 0.57 mmol) was recrystallised by slow evaporation of dichloromethane at -25 °C).



Procedure

Silver carbonate (0.166 g, 0.60 mmol) was added to a solution of (*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate (0.250 g, 0.60 mmol) in dichloromethane (13 mL) and stirred for 5 min. A suspension of triphenylphosphinegold chloride (0.297 g, 0.60 mmol) in dichloromethane (2 mL) was added to the solution of (*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate and silver carbonate and stirred for 35 min. The reaction mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as white solid (0.402 g, 94%).

Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate (130b)



Appearance: yellow solid **Yield:** 97%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.60 – 7.44 (15H, m, Ar-H), 4.71 – 4.64 (1H, m, 2-H), 3.72 (3H, s, 6-H), 1.96 (1H, td, *J*=6.6, 13.3, 5-H), 1.87 – 1.64 (2H, m, 4-H), 0.95 (3H, t, *J*=6.8, 8-H), 0.91 (3H, d, *J*=6.8, 7-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.8 (3-C), 134.2 (Ar-CH), 134.1 (Ar-CH), 131.9 (Ar-C), 131.9 (Ar-CH), 129.3 (Ar-CH), 129.2 (Ar-CH), 129.0 (1-CF), 128.5 (1-CF), 58.9 (2-CH), 51.9 (6-CH_3), 46.2 (4-CH_2), 24.0 (5-CH), 23.2 (7-CH_3), 21.4 (8-CH_3).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 31.57 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2955 (ar CH st), 2460 (Ar comb), 1744 (C=O st), 1213 (CO-O st), 1173 (S-O st as), 1102 (S-O st sy).

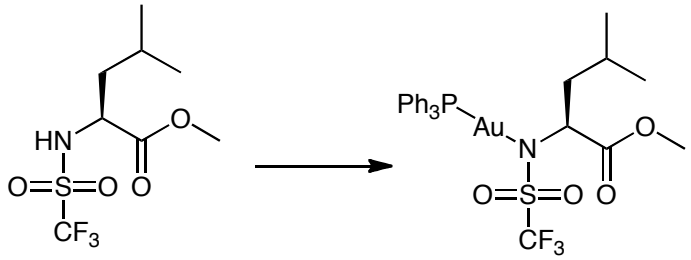
$[\alpha]_D^{26}$=4.1 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{26}H_{28}AuF_3NO_4PSNa$

Found: 758.0987 m/z *Err[ppm]: -0.05*

Calculated: 758.0986 m/z

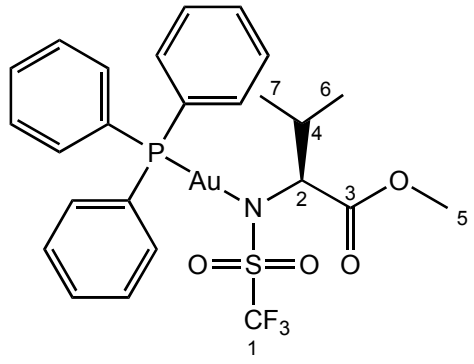
X-Ray: see appendix **130b** (The complex (30 mg, 0.041 mmol) was recrystallised by slow diffusion of dichloromethane (0.1 mL) into pentane (0.4 mL) at +5 °C).



Procedure

Silver carbonate (0.149 g, 0.54 mmol) was added to a solution of methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate (0.150 g, 0.54 mmol) in dichloromethane (13.5 mL) and stirred for 5 min. The solution of triphenylphosphinegold chloride (0.268 g, 0.54 mmol) was added to the solution of methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate and silver carbonate and stirred for 35 min. The reaction mixture was filtered through Celite and the solvent concentrated under reduced pressure to give the corresponding compound as yellow solid (0.386 g, 97%).

Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-valinate (130c)



Appearance: yellow solid **Yield:** 91%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.60 – 7.45 (15H, m, Ar), 4.31 – 4.26 (1H, m, 2-H), 3.73 (3H, s, 5-H), 2.20 – 2.11 (1H, m, 4-H), 1.17 (3H, d, *J*=6.8, 7-H), 0.99 (3H, d, *J*=6.7, 6-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.4 (3-C), 134.2 (Ar), 134.1 (Ar), 131.8 (Ar), 129.3 (Ar), 129.2 (Ar), 129.1 (1-CF), 128.6 (1-CF), 66.8 (2-CH), 51.6 (5-CH_3), 34.2 (4-CH), 19.2 (7-CH_3), 19.1 (6-CH_3).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 31.57 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2963 (ar CH st), 1734 (C=O st), 2200 (Ar comb), 1211 (CO-O st), 1174 (S-O st as), 1103 (S-O st sy).

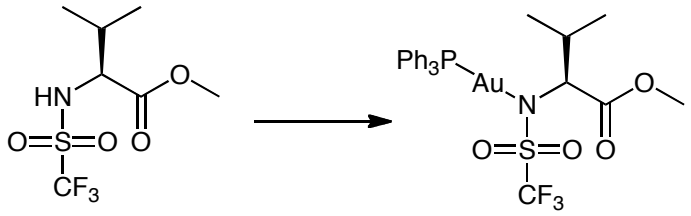
$[\alpha]_D^{26}$=12.5 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{25}H_{26}AuF_3NO_4PSNa$

Found: 744.0861 m/z *Err[ppm]: -4.15*

Calculated: 744.0830 m/z

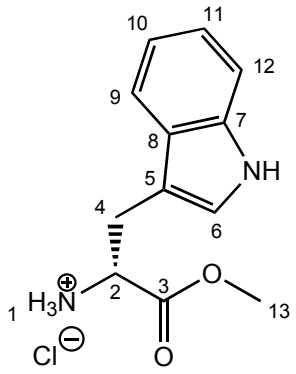
X-Ray: see appendix **130c** (The complex (0.376 g, 0.52 mmol) was recrystallised by slow evaporation of dichloromethane at -25 °C)



Procedure

Silver carbonate (0.157 g, 0.57 mmol) was added to a solution of methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-valinate (0.150 g, 0.57 mmol) in dichloromethane (14.25 mL) and stirred for 5 min. The solution of triphenylphosphinegold chloride (0.282 g, 0.57 mmol) was added to the solution of methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-valinate and silver carbonate and stirred for 35 min. The reaction mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as yellow solid (0.376 g, 91%).

(2*R*)-3-(1*H*-indol-3-yl)-1-methoxy-1-oxopropan-2-aminium chloride (132d)



Appearance: white solid **Yield:** 86%

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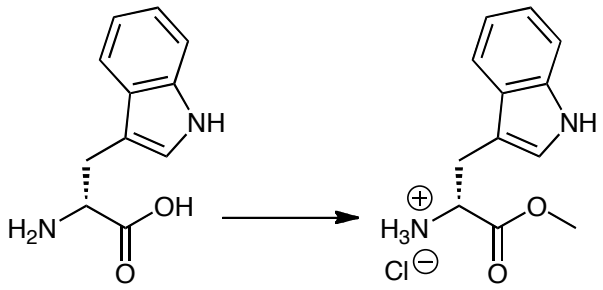
^{1}H NMR (500 MHz, D_2O) δ = 7.52 (1H, d, *J*=7.9, 9-H), 7.46 (1H, d, *J*=8.1, 12-H), 7.26 – 7.10 (3H, m, 4, 5, 9-H), 4.37 (1H, t, *J*=6.0, 2-H), 3.73 (3H, s, 13-H), 3.44 – 3.31 (2H, m, 4-H).

^{13}C NMR (126 MHz, D_2O) δ = 170.4 (2-C), 136.3 (7-C), 126.4 (8-C), 125.4 (6-C), 122.3 (11-CH), 119.6 (10-CH), 118.1 (9-CH), 112.1 (12-CH), 106.0 (5-C), 53.6 (13-CH_3), 53.3 (2-CH), 25.7 (4-CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 3261 (NH st), 2870 (N^+-H st), 2023 (Ar comb), 1748 (C=O st), 1229, 1211 (CO-O st as), 1181 (C-O st as).

$[\alpha]_D^{23}$=−15.2 (*c*=1.0 in water).

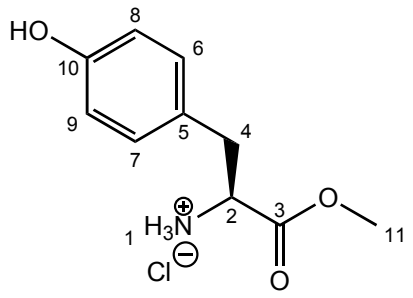
Acc. Mass (FAB): $C_{12}H_{15}N_2O_2$
Found: 219.1120 m/z *Err[ppm]: 3.59*
Calculated: 219.1128 m/z



Procedure

Thionyl chloride (9.87 mmol, 0.72 mL) was added dropwise to the solution of (*D*)-tryptophan (1.000 g, 4.89 mmol) in methanol (33 mL). The reaction was heated to reflux with vigorous agitation for 24 h. After cooling, the reaction mixture was concentrated under reduced pressure and the residual methanol traces were removed by azeotropic distillation with dichloromethane (10 mL) under reduced pressure to give the title compound as a white solid (1.070 g, 86%).

(2*S*)-3-(4-hydroxyphenyl)-1-methoxy-1-oxopropan-2-aminium chloride (132e)



Appearance: white solid **Yield:** 99%

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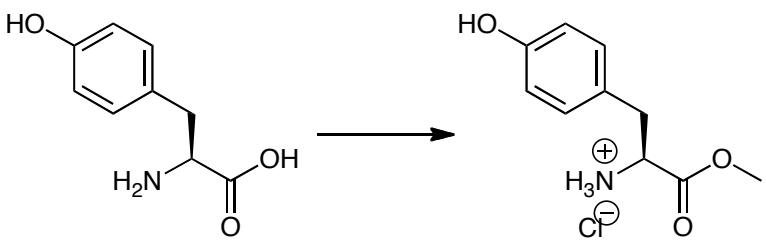
^{1}H NMR (500 MHz, D_2O) δ = 7.08 (2H, d, *J*=7.7, 6, 7-H), 6.83 (2H, d, *J*=7.7, 8, 9-H), 4.31 (1H, t, *J*=5.9, 2-H), 3.76 (3H, s, 11-H), 3.24 – 3.02 (2H, m, 4-H).

^{13}C NMR (126 MHz, D_2O) δ = 170.1 (2-C), 155.2 (10-C), 130.8 (6, 7-CH), 125.4 (5-C), 116.0 (8, 9-CH), 54.2 (2-CH), 53.5 (11-CH_3), 34.8 (4-CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 3335 (NH st), 2877 (N^+-H st), 1983 (Ar comb), 1741 (C=O st), 1225 (CO-O st as), 1199 (C-O st as).

$[\alpha]_D^{23}$=−4.7 (*c*=1.0 in water).

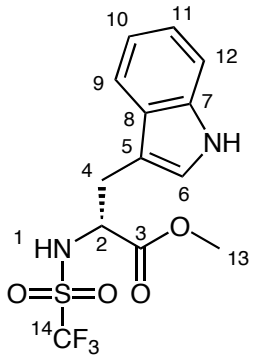
Acc. Mass (FAB): $C_{10}H_{14}NO_3$
Found: 196.0962 m/z *Err[ppm]: 3.27*
Calculated: 196.0968 m/z



Procedure

Thionyl chloride (6.62 mmol, 0.48 mL) was added dropwise to the solution of (*L*)-tyrosine (0.600 g, 3.31 mmol) in methanol (22 mL). The reaction was heated to reflux with vigorous agitation for 24 h. After cooling, the reaction mixture was concentrated under reduced pressure and the residual methanol traces were removed by azeotropic distillation with dichloromethane (10 mL) under reduced pressure to give the title compound as a white solid (0.646 g, 84%).

Methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate (133d)



Appearance: brown-yellow solid **Yield:** 90%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 (1H, s, NH-1), 7.52 (1H, d, *J*=7.9, 9-H), 7.37 (1H, d, *J*=8.1, 12-H), 7.24 – 7.19 (1H, m, 10-H), 7.17 – 7.12 (1H, m, 11-H), 7.04 (1H, d, *J*=2.3, 1H, 6-H), 4.57 (1H, t, *J*=5.0, 1H, 2-H), 3.71 (3H, s, 13-H), 3.38 (2H, m, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.7 (3-C), 136.2 (7-C), 127.1 (8-C), 124.6 (14-CF), 123.5 (6-CH), 123.3 (14-CF), 122.5 (11-CH), 120.7 (14-CF), 120.0 (10-CH), 118.3 (9-CH), 118.2 (14-CF) 115.6 (14-CF), 111.4 (12-CH), 108.0 (5-C), 57.4 (2-CH), 53.0 (13-CH_3), 29.3 (4-CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 3402.9 (ar NH st), 3261.5 (NH st), 2197.0, 2157.2, 1031.4 (Ar comb), 1712.6 (C=O st), 1230.6 (CO-O st),1185.0 (S-O st as), 1145.5 (S-O st sy).

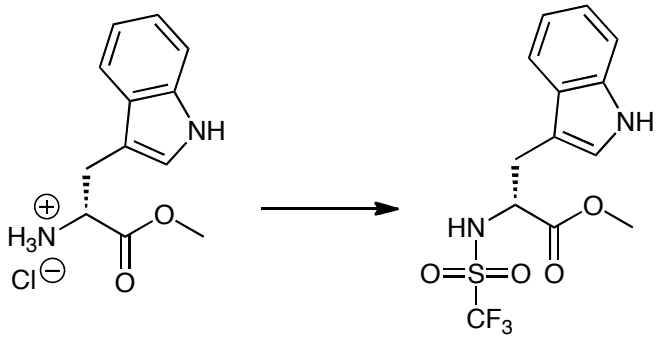
$[\alpha]_D^{26}$=−31.8 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{13}H_{13}F_3N_2O_4SNa$

Found: 373.0446 m/z *Err[ppm]: -1.47*

Calculated: 373.0440 m/z

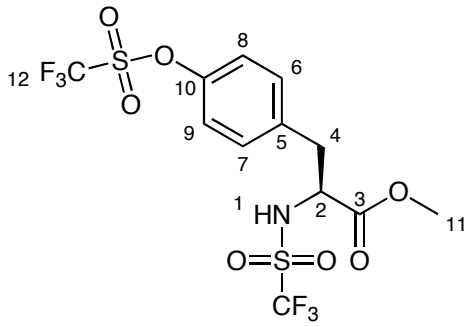
Rf (diethyl ether): 0.84 (green, PMA dip)



Procedure

A solution of triflic anhydride (1.382 g, 4.89 mmol) in dichloromethane (4.9 mL) was dripped into a solution of (2*R*)-3-(1*H*-indol-3-yl)-1-methoxy-1-oxopropan-2-aminium chloride (1.073 g, 4.89 mmol) and triethylamine (1.487 g, 14.69 mmol) in dichloromethane (18.9 mL) at -78 °C. The mixture was stirred for 24 h at room temperature. Water (5 mL) was added and the pH was adjusted to pH=5 using conc. hydrochloric acid. The aqueous layer extracted with diethyl ether. The organic extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as brown-yellow solid (1.548 g, 90%).

(*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido)propanoate (133e)



Appearance: yellow solid **Yield:** 49%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 – 7.22 (4H, m, 6, 7, 8, 9-H), 4.49 (1H, t, *J*=6.0, 1H, 2-H), 3.78 (3H, s, 11-H), 3.23 – 3.13 (2H, m, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 170.4 (3-C), 149.2 (10-C), 134.8 (5-C), 131.3 (6, 7-CH), 123.1 (12-CF), 121.8 (8, 9-CH), 120.6 (12-CF), 120.0 (12-CF), 118.0 (12-CF), 117.4 (12-CF), 115.8 (12-CF), 57.7 (2-CH), 53.2 (11-CH_3), 38.9 (4-CH_2).

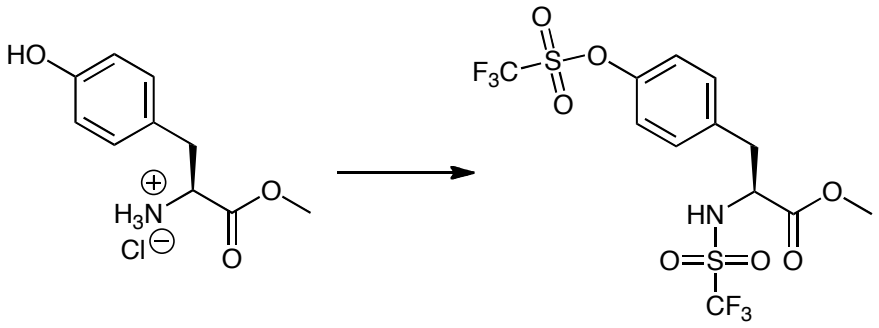
IR (diamond, ν_{MAX}, cm^{-1}) 3349 (O-H st), 3221 (NH st), 2176 (Ar comb), 1724 (C=O st), 1238 (CO-O st), 1199 (S-O st as), 1141 (S-O st sy).

$[\alpha]_D^{26}$=17.1 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{14}H_{10}F_6NO_7S_2$
Found: 481.9778 m/z *Err[ppm]: 4.08*
Calculated: 481.9797 m/z

Rf (diethyl ether): 0.94 (black-brown, PMA dip)

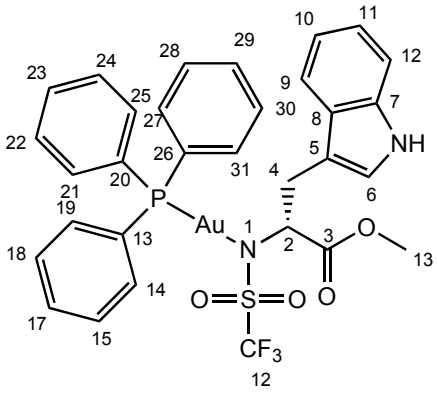
X-Ray: see appendix **133e** (The complex (0.300 g, 0.65 mmol) was recrystallised by slow evaporation of diethyl ether at room temperature).



Procedure

A solution of triflic anhydride (0.934 g, 3.31 mmol) in dichloromethane (3.31 mL) was dripped into a solution of (2*S*)-3-(4-hydroxyphenyl)-1-methoxy-1-oxopropan-2-aminium chloride (0.767 g, 3.31 mmol) and triethylamine (1.005 g, 9.93 mmol) in dichloromethane (12.79 mL) at -78 °C. The mixture was stirred for 24 h at room temperature. Water (5 mL) was added and the pH was adjusted to pH=5 using conc. hydrochloric acid. The aqueous layer extracted with diethyl ether. The organics extracts were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as yellow solid (0.704 g, 49%).

Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate (130d)



Appearance: yellow solid **Yield:** 99%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 – 6.97 (20H m, Ar), 5.06 (1H, q, *J*=6.1, 2-H), 3.65 (3H, s, 13-H), 3.51 – 3.26 (2H, m, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.1 (3-C), 135.9 (7-C), 134.2 (Ar), 134.10 (Ar), 131.7 (Ar), 131.7 (Ar), 129.1 (Ar), 129.0 (Ar), 128.6 (Ar), 127.8 (8-CH), 123.7 (6-CH), 122.0 (11-CH), 119.4 (10-CH), 119.0 (9-CH), 111.1 (12-CH), 110.5 (5-C), 60.8 (2-CH), 52.0 (13-CH_3), 31.7 (4-CH).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 31.01 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 3398 (ar NH st), 2180 (Ar comb), 1738 (C=O st), 1212 (CO-O st), 1176 (S-O st as), 1101 (S-O st sy).

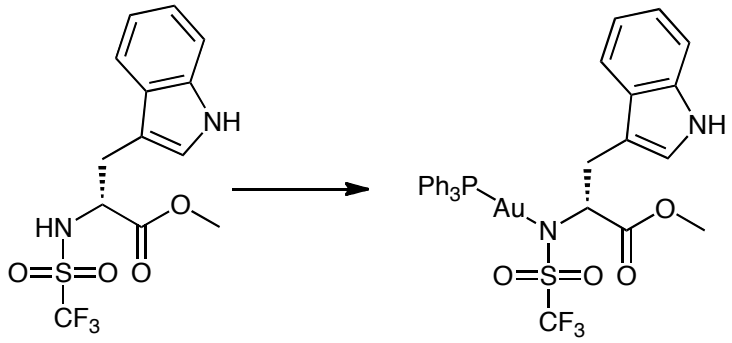
$[\alpha]_D^{24}$=−42.5 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{31}H_{27}AuF_3N_2O_4PSNa$

Found: 831.0944 m/z *Err[ppm]: -0.56*

Calculated: 831.0939 m/z

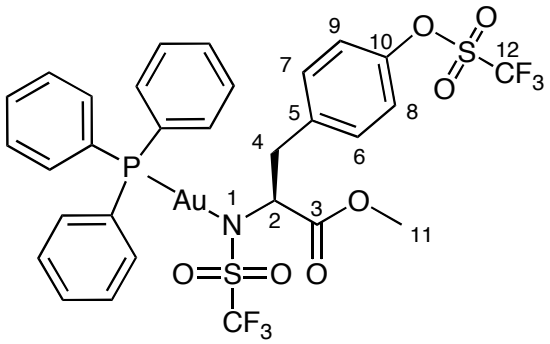
X-Ray: see appendix **130d** (The complex (30 mg, 0.038 mmol) was recrystallised by slow diffusion of chloroform (0.1 mL) into benzene (0.4 mL) at +5 °C).



Procedure

Silver carbonate (38.6 mg, 0.143 mmol) was added to the solution of methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate (50 mg, 0.143 mmol) in dichloromethane (3.57 mL) and stirred for 5 min. Triphenylphosphine gold chloride (70.6 mg, 0.143 mmol) was added to the solution of methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate and silver carbonate and stirred for 48 h. The reaction was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as pale yellow solid (0.115 g, 99%).

Triphenylphosphine gold (*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido)propanoate (130e)



Appearance: white solid **Yield:** quantitative

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 – 7.44 (15H, m, Ar), 7.27 (2H, d, *J*=9.6, 6, 7-H), 7.00 (2H, d, *J*=8.6, 2H, 8, 9-H), 4.91 (1H, m, 2-H), 3.67 (3H, s, 11-H), 3.26 – 3.16 (2H, m, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.9 (3-C), 148.4 (10-Ar), 137.0 (5-Ar), 134.2 (Ar), 134.1 (Ar), 132.01 (Ar), 131.5 (6, 7-Ar), 129.3 (Ar), 129.2 (Ar), 121.0 (8, 9-Ar), 61.5 (2-CH), 52.0 (11-CH_3), 41.7 (4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 31.30 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2956 (O-H st), 2073 (Ar comb), 1738 (C=O st), 1249 (CO-O st), 1176 (S-O st as), 1137 (S-O st sy).

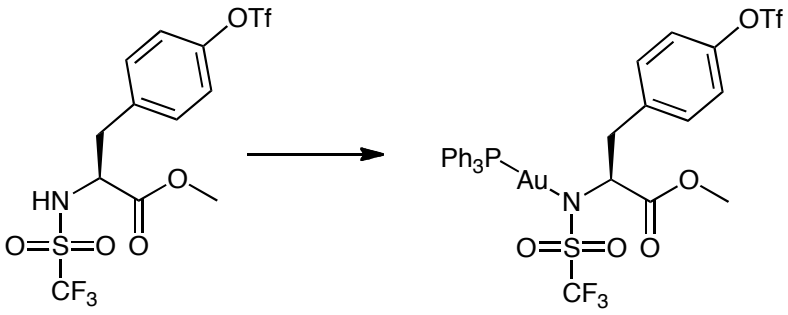
$[\alpha]_D^{24}$=2.0 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{30}H_{25}AuF_6NO_7PS_2$

Found: 940.0383 m/z *Err[ppm]: -11.84*

Calculated: 940.0272 m/z

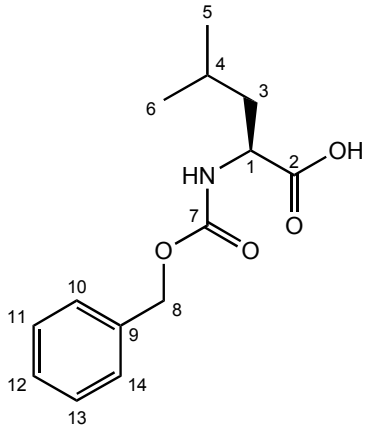
X-Ray: see appendix **130e** (The complex (30 mg, 0.033 mmol) was recrystallised from dichloromethane (0.1 mL) into pentane (0.4 mL) at -25 °C).



Procedure

Silver carbonate (68.6 mg, 2.49 mmol) was added to the solution of (*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido)propanoate (114.2 mg, 2.49 mmol) in dichloromethane (6.2 mL) and stirred for 5 min. A solution of gold triphenylphosphine chloride (123.1 mg, 2.49 mmol) was added to the solution of (*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido) propanoate and silver carbonate and stirred for a further 24 h. The reaction was filtered through Celite and solvent was evaporated under reduced pressure to give the corresponding compound as white solid (0.228 g, quantitative).

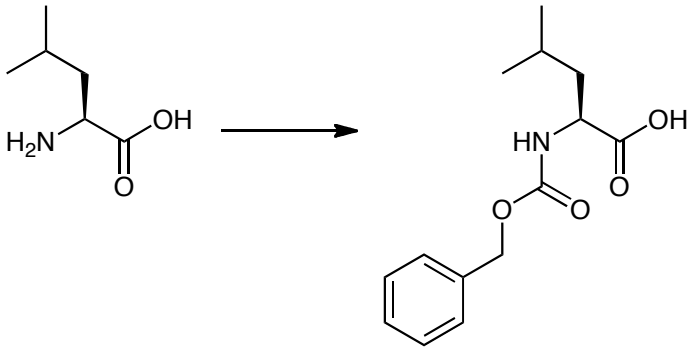
N-benzoxycarbonyl-(*L*)-leucine (145)



Appearance: colourless oil **Yield:** 76%

All data is identical to that reported.[96]

Rf (diethyl ether): 0.75 (grey, PMA dip)

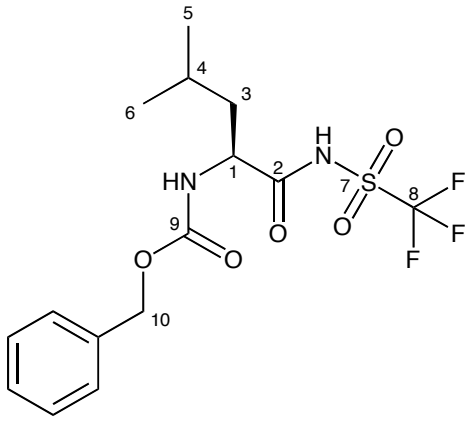


Procedure

To a solution of (*L*)-leucine (0.400 g, 3.05 mmol) in 2M sodium hydroxide aq. (3.75 mL) cooled to 0 °C, benzyl chloroformate (3.54 mmol, 0.52 mL) was added dropwise over 15 min. The mixture was stirred at room temperature for another 2 h, and then acidified (pH

= 3) with conc. hydrochloric acid. The aqueous layer was extracted with ethyl acetate (3x10 mL). The combined organic layers were dried over anhydrous magnesium sulphate and filtered. The solvent was evaporated under reduced pressure to give the corresponding compound colourless oil (0.614 g, 76%).

N^2-[(benzyloxy)carbonyl}-N^1-[(trifluoromethyl)sulfonyl]-(*L*)-leucinamide (147)



Appearance: white solid **Yield:** 53%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 – 7.16 (5H, m, Ar), 5.56 (1H, s, NH), 5.25 – 4.80 (2H m, 3-H), 4.06 (1H, s, 1-H), 3.69 (1H, br s, NH), 1.63 – 1.32 (3H m, 3, 4-H), 0.81 (6H, s, 5,6-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 181.7 (2-C), 157.3 (9-C), 135.8 (11-C(Ar)), 128.4 (12,14,16-CH(Ar)), 128.1 (8-CF_3), 127.8 (13,15-CH(Ar)), 67.3 (10-CH_2), 56.8 (1-CH), 40.8 (3-CH_2), 24.6 (4-CH), 22.7 (6-CH_3), 21.6 (5-CH_3).

IR (diamond, ν_{MAX}, cm^{-1}) 3393 (NH st), 2020 (Ar comb), 1704, 1622 (C=O st amide), 1292 (CO-O st), 1181 (S-O st as), 1124 (S-O st sy).

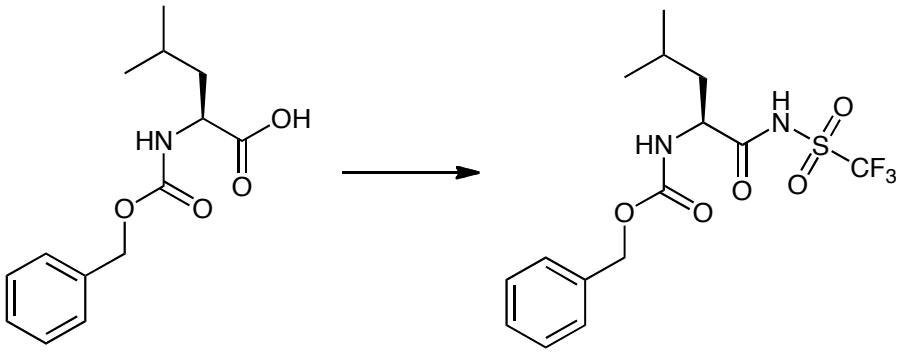
$[\alpha]_D^{22}$=41.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{15}H_{19}F_3N_2O_5SNa$

Found: 419.0860 m/z *Err[ppm]: -0.26*

Calculated: 419.0859 m/z

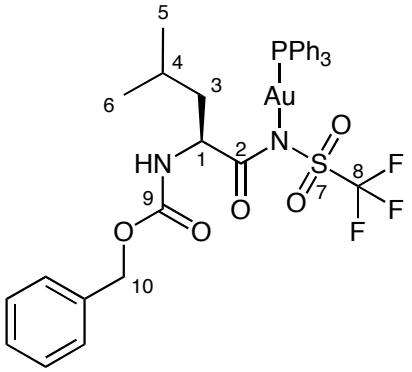
Rf (diethyl ether): 0.26 (blue, PMA dip)



Procedure

N-benzoxycarbonyl-(*L*)-leucine (0.100 g, 0.377 mmol), triflic amine (56.2 mg, 0.377 mmol) and HOBt•H_2O (57.7 mg, 0.377 mmol) were dissolved in dichloromethane and cooled to 0 °C. EDC (60.0 mg, 0.386 mmol) was added and mixture stirred for 15 min at 0 °C and then at room temperature for a further 3 days. The precipitate was filtered off and the filtrate concentrated under reduced pressure. The residue was dissolved in ethyl acetate (5 mL) and washed with 1M citric acid (3mL), saturated solution of sodium carbonate (3 mL), brine (3 mL) and dried over anhydrous magnesium sulphate and filtered. The organic layer was concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as white solid (79.4 mg, 53%).

Triphenylphosphine gold N^2-[(benzyloxy)carbonyl}-N^1-[(trifluoromethyl)sulfonyl]-(*L*)-leucinamide (150)



Appearance: white solid **Yield:** 74% (from ^{31}P NMR)

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^{1}H NMR (500 MHz, $CDCl_3$) δ = δ = 7.64 – 7.28 (20H, m, Ar), 5.16 – 4.97 (3H m, 10,1-H), 1.87 – 1.66 (2H m, 3, 4-H), 1.61 – 1.52 (1H m, 3-H), 0.86 (3H, d, *J*=6.5, 5-H), 0.73 (3H, d, *J*=5.9, 6-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.2 (2-C), 155.9 (9-C), 136.39 (s, Ar), 134.3 (s, Ar), 134.2 (s, Ar), 134.1 (s, Ar), 132.3 (s, Ar), 132.3 (s, Ar), 132.1 (s, Ar), 132.0 (s, Ar), 131.9 (s, Ar), 131.9 (s, Ar), 131.57 (s, Ar), 129.5 (s, Ar), 129.4 (s, Ar), 129.2 (s, Ar), 129.1 (s, Ar), 129.0 (s, Ar), 128.8 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 127.99 (s, Ar), 127.83 (s, Ar), 127.48 (s, Ar), 127.35 (s, Ar), 124.29 (s, 8-CF), 121.71 (s, 8-CF), 119.13 (s, 8-CF), 116.54 (s, 8-CF), 66.8 (10-CH_2), 55.8 (1-CH), 43.0 (3-CH_2), 24.7 (4-CH), 23.2 (6-CH_3), 21.6 (5-CH_3).

^{31}P NMR (161 MHz, $CDCl_3$) δ 31.1(26%), 30.6(74%).

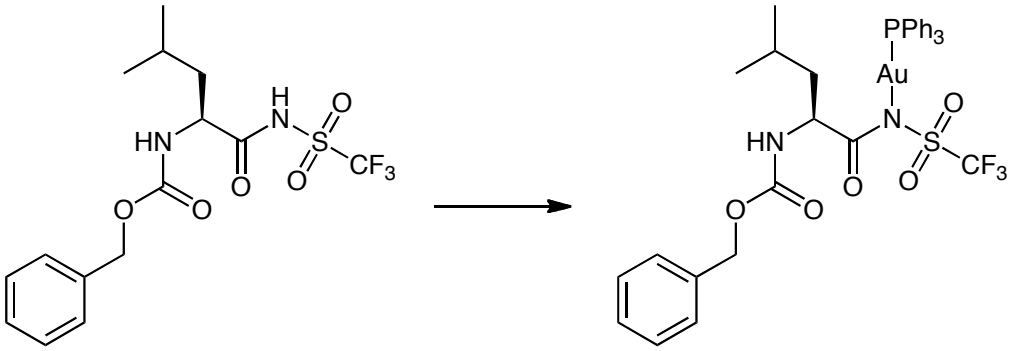
IR (diamond, ν_{MAX}, cm^{-1}) 3316 (NH st), 1982 (Ar comb), 1702 (C=O st amide), 1310 (CO-O st), 1180 (S-O st as), 1121 (S-O st sy).

$[\alpha]_D^{25}$= 29.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{33}H_{33}AuF_3N_2O_5PS$

Found: 877.1453 m/z *Err[ppm]: -10.85*

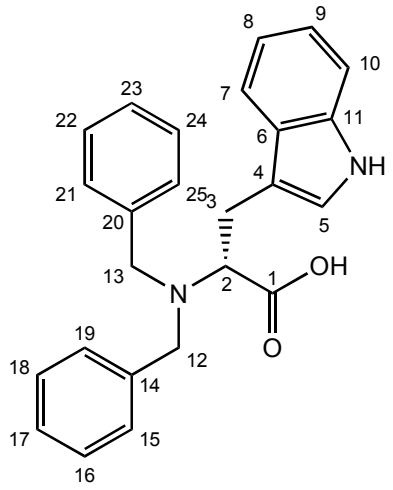
Calculated: 877.1385 m/z



Procedure

Silver carbonate (0.126 g, 0.46 mmol) was added to a solution of (*S*)-benzyl (4-methyl-1-oxo-1-(trifluoromethylsulfonamido)pentan-2-yl)carbamate (0.100 g, 0.25 mmol) in dichloromethane (C=0.1M, 2.52 mL) at 0 °C and stirred for 5 min. Triphenylphosphinegold chloride (0.125 g, 0.25 mmol) was added and the resultant mixture stirred for 2 days at 0 °C. The reaction mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as pink solid (0.222 g, 74% from ^{31}P NMR).

N,*N*-dibenzyl-(*D*)-tryptophan (154)



Appearance: white solid **Yield:** Procedure: A=12%, B=43%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.06 (1H, s, NH), 7.45 – 6.93 (15H, m, Ar), 3.92 (1H, t, *J*=7.0, 2-H), 3.95 – 3.68 (4H, m, 12, 13-H), 3.57 – 3.12 (2H, m, 3-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.1 (1-C), 137.6 (14, 20-C), 136.1 (11-C), 128.9 (16, 18, 22, 24-CH), 128.4 (15, 19, 21, 25-CH), 127.4 (17, 22-CH), 127.1 (6-C), 122.9 (5-CH), 122.0 (9-CH), 119.3 (8-CH), 118.7 (7-CH), 111.9 (10-CH), 111.1 (4-C), 61.9 (2-CH), 54.6 (12, 13-CH_2), 24.1 (3-CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 3403 (Ar NH st), 2924 (O-H st), 2020 (Ar comb), 1702 (C=O st), 1203 (CO-O st).

$[\alpha]_D^{21}$=48.0 (*c*=1.0 in dichloromethane).

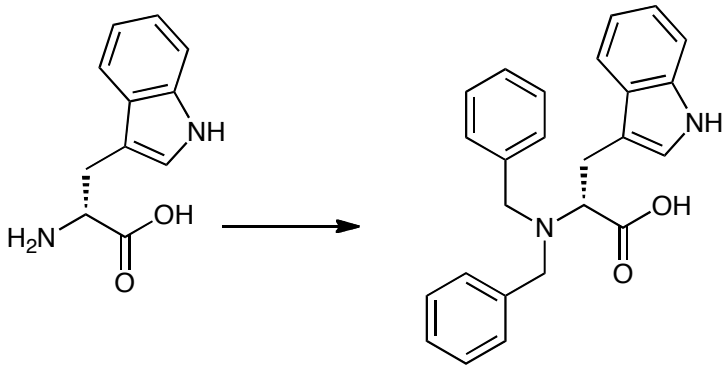
Acc. Mass (FAB): $C_{25}H_{25}N_2O_4$

Found: 385.1911 m/z *Err[ppm]: -0.50*

Calculated: 385.1916 m/z

X-Ray: see appendix **154** (The complex (30 mg, 0.078 mmol) was recrystallised from diethyl ether at +5 °C).

Rf (diethyl ether : PET, [50:50]): 0.32 (black, PMA dip)



Procedure A

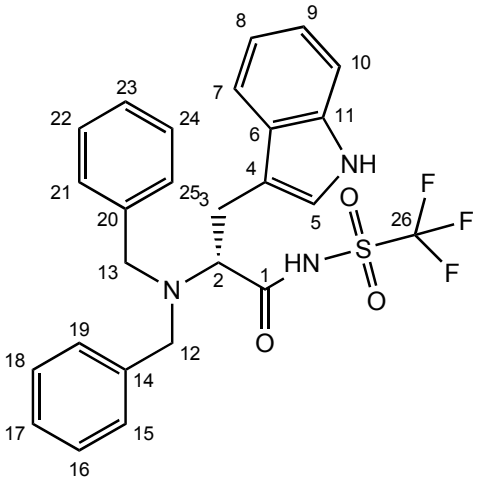
Benzaldehyde (1.214 g, 11.44 mmol) was added to a solution of (*D*)-tryptophane (0.778 g, 3.81 mmol) in phosphate buffer (pH=7, 59 mL) and stirred for 5 minutes at room temperature. Sodium cyanoborohydride (0.631 g, 9.53 mmol) was added and the mixture stirred for 3 days. The mixture was extracted with diethyl ether (3x30 mL). The combined organic layers were filtered. The separation was repeated. The combined organic layers were dried over magnesium sulphate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether: PET [50:50]) afforded the title compound as white solid (0.179 g, 12%).

Procedure B

(*D*)-tryptophan (1.250 g, 6.12 mmol) was added to a solution of potassium carbonate (1.185 g, 8.57 mmol) in a 1:1 mixture of water and ethanol (10 mL). The solution was heated to reflux and benzyl chloride (1.628 g, 12.86 mmol, 1.48 mL) was added portionwise over 10 minutes. The reaction was refluxed for a further 1 h and then concentrated to 1.6 mL, followed by addition of acetic acid (0.037 mL). The reaction was

extracted with dichloromethane (3x15 mL). The combined organic layers were dried over magnesium sulphate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether : PET, [50:50],) afforded the title compound as white solid (1.000 g, 43%).

N,*N*-dibenzyl-*N*[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide (156)



Appearance: white solid **Yield:** 73%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.45 (1H, br s, NH), 7.37 – 6.82 (15H, m, Ar), 4.09 – 3.51 (6H, m, 12, 13, 3 -H), 1.27 (1H, dd, *J*=8.4, 15.0,, 3-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.9 (s, 1-C) 136.3 (s, Ar), 129.1 (d, *J*=18.25 Ar), 126.5 (s, Ar), 123.8 (s, Ar), 122.3 (s, Ar), 121.4 (s, Ar), 119.6 (s, Ar), 118.9 (s, Ar), 118.4 (s, Ar), 111.7 (s, Ar), 64.9 (s, 2-CH), 54.7 (s, 12, 13-CH_2), 29.7 (s, 3- CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 3403.21 (Ar NH st), 2919.69 (NH st), 2019.56 (Ar comb), 1619.39 (C=O st amide), 1179.12, 1180.95 (S-O st as), 1125.62 (S-O st sy).

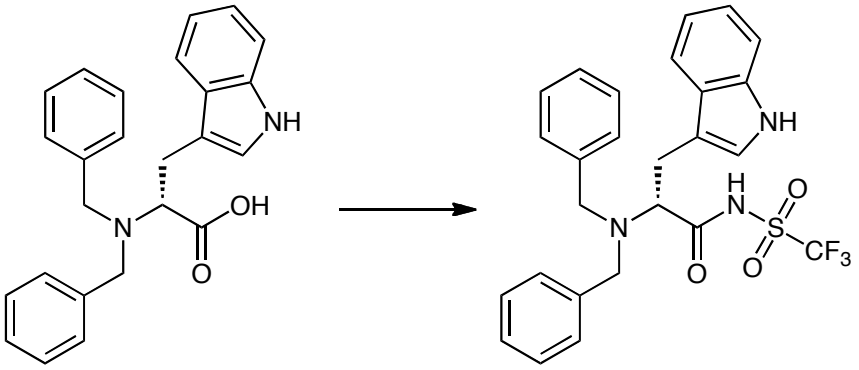
$[\alpha]_D^{21}$=39.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{26}H_{24}F_3N_3O_3SNa$

Found: 538.1398 m/z *Err[ppm]: -2.84*

Calculated: 538.1383 m/z

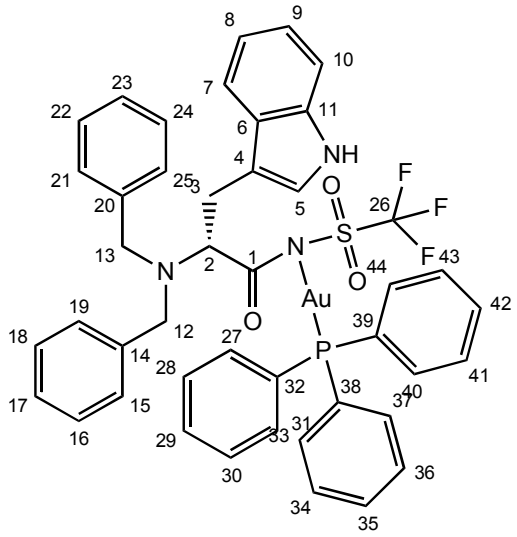
Rf (diethyl ether): 0.23 (dark brown, PMA dip)



Procedure

N,*N*-dibenzyl-(*D*)-tryptophan (0.152 g, 0.40 mmol), triflic amine (58.9 mg, 0.40 mmol) and HOBt•H_2O (60.5 mg, 0.40 mmol) were dissolved in dichloromethane (1.05 mL) at 0 °C. EDC (60.0 mg, 0.40 mmol) was added and the mixture stirred for 15 min and then at room temperature for a further 3 days. The precipitate was filtered off and the filtrate evaporated under reduced pressure. The residue was dissolved in 5 mL of ethyl acetate and washed with 1 M citric acid, saturated sodium bicarbonate, brine, dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as white solid (0.149 g, 73%).

Triphenyphosphine gold *N*,*N*-dibenzy-*N*[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide (157)



Appearance: green solid **Yield:** 90% from ^{31}PNMR

Product not pure

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61 – 6.67 (36H m, Ar), 4.26 (1H s, 2-H), 4.16 (2H d, *J*= 14.3, 12, 13-H), 3.80 (2H, d, *J*= 14.3, 12, 13-H), 3.57 (2 H, dd, *J*=9.8, 14.0, 3-H), 3.12 (2 H, dd, *J*=4.5, 14.1, 3-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.9 (s, 1-C), 140.1 (s, Ar), 135.7 (s, 11-C), 134.07 (d, *J*=13.7, Ar), 131.9 (s, Ar), 129.1 (d, *J*=12.1, Ar), 128.9 (s, Ar), 128.1 (s, Ar), 128.0 (s, Ar), 127.5 (s, Ar), 127.3 (s, Ar), 126.8 (s, 6-C), 123.2 (s, 5-CH), 121.7 (s, 9-CH), 119.3 (s, 8-CH), 118.9 (s, 7-CH), 112.2 (s, 10-CH), 110.7 (s, 4-CH), 67.2 (s, 2-CH), 54.7 (s, 12, 13-CH_2), 26.8 (s, 3-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.00 (s, 1), 29.92 (s, 11).

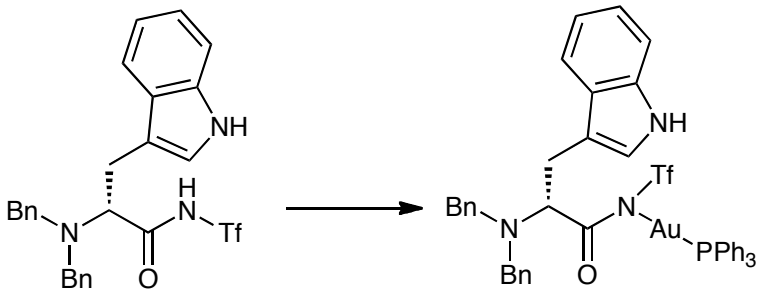
IR (diamond, ν_{MAX}, cm^{-1}) 2920 (NH st), 2019.56 (Ar comb), 1685 (C=O st amide), 1437 (H-C-H st as) 1181 (S-O st as), 1101 (S-O st sy).

$[\alpha]_D^{21}$=57.7 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{44}H_{39}AuF_3N_3O_3PSNa$

Found: 974.2110 m/z *Err[ppm]: -4.95*

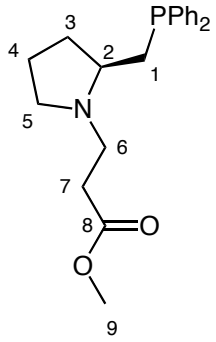
Calculated: 974.2062 m/z



Procedure

Silver carbonate (0.110 g, 0.40 mmol) was added to a solution of *N*,*N*-dibenzyl-*N*[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide (0.114 g, 0.22 mmol) in dichloromethane (2.52 mL) at 0 °C and stirred for 5 min. Triphenylphosphine gold chloride (0.110 g, 0.22 mmol) was added and the reaction mixture stirred for a further 2 days at 10 °C. The reaction was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as green solid (0.214 g, 90%).

Methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl} propanoate (194)



Appearance: yellow cloudy viscous oil **Yield:** 47%

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^{1}H NMR (500 MHz, cdcl3) δ = 7.50 – 7.39 (4H, m, Ar), 7.37 – 7.28 (6H, m, Ar), 3.66 (3H, s, 9-H), 3.19 – 3.03 (2H, m, 5, 6-H), 2.54 (1H, dt, *J*=3.3, 13.3, 4-H), 2.49 – 2.29 (4H, m, 6, 7-H), 2.15 – 2.06 (1H, m, 5-H), 2.06 – 1.91 (2H, m, 1, 3-H), 1.83 – 1.53 (3H, m, 3, 4-H).

^{13}C NMR (126 MHz, cdcl3) δ = 172.7 (s, 8-C), 139.3 (d, *J*=12.1, Ar), 138.5 (d, *J*=13.3, Ar), 133.0 (d, *J*=19.3, Ar), 132.6 (d, *J*=18.7, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 128.3 (s, Ar), 62.1 (d, *J*=19.3, 2-CH), 53.4 (d, *J*=0.8, 5-CH_2), 51.5 (s, 9-CH_3), 49.1 (s, 6-CH_2), 33.6 (d, *J*=13.3, 1-CH_2), 33.5 (s, 7-CH_2), 31.7 (d, *J*=7.8, 3-CH_2), 22.1 (d, *J*=0.6, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -21.19.

IR (diamond, ν_{MAX}, cm^{-1}) 2961, 2802 (CH_3O st), 1735 (C=O st), 1433 (H-C-H st as), 1175 (C-O st as).

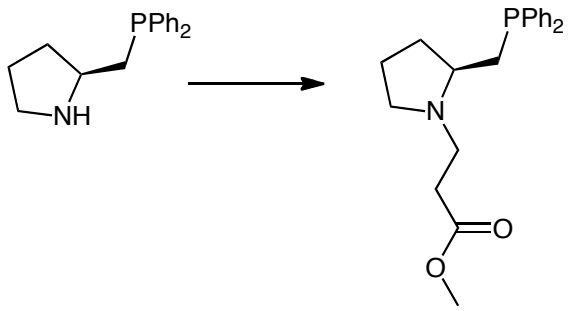
$[\alpha]_D^{26}$=−78.2 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{21}H_{27}NO_2P$

Found: 356.1778 *error [ppm]: -1.28*

Calculated: 356.1774

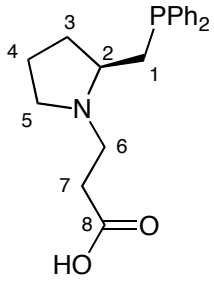
Rf (methanol : dichloromethane, [5:95]): 0.51 (blue, PMA dip)



Procedure

A solution of methyl-3-bromopropionate (1.55 g, 9.28 mmol, 1.01 mL) in dichloromethane (8.0 mL) was added dropwise to a solution of triethylamine (1.88 g, 18.57 mmol, 2.61 mL) and (2*S*)-2-[(diphenylphosphino)methyl]pyrrolidine (2.50 g, 9.28 mmol) in dichloromethane (27 mL). The resultant solution was stirred at 30 °C overnight. The reaction mixture was poured into water/dichloromethane (1:1, 200 mL). The crude residue was extracted with dichloromethane (100 mL), the organic phase was washed with water (100 mL), brine (100 mL) and then dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (methanol : dichloromethane, [5:95]) afforded the title compound as a yellow cloudy viscous oil (1.57 g, 47%).

3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}propanoic acid (195)



Appearance: yellow cloudy viscous oil **Yield:** quantitative

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (1H, br s, OH), 7.40 (10H, m, Ar), 3.70-3-80 (1H, m, 5-H), 3.61 – 3.49 (1H, m, 7-H), 3.06 – 2.72 (6H, m, 1, 6, 7, 5-H), 2.64 (1H, t, *J*=12.1, 1-H), 2.24 – 1.82 (m, 4H, 3, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.2 (s, 8-C), 136.8 (d, *J*=11.3, Ar), 136.1 (d, *J*=12.7, Ar), 133.0 (d, *J*=20.2, Ar), 132.5 (d, *J*=19.2, Ar), 129.6 (s, Ar), 129.1 (s, Ar), 128.9 (d, *J*=7.3, Ar), 128.7 (d, *J*=6.9, Ar), 66.9 (d, *J*=23.2, 2-CH), 52.8 (s, 5-CH_2), 49.4 (s, 7-CH_2), 31.1 (s, 6-CH_2), 30.5 (d, *J*=7.4, 3-CH_2), 29.6 (d, *J*=16.2, 1-CH_2), 21.7 (s, 4-CH_2).

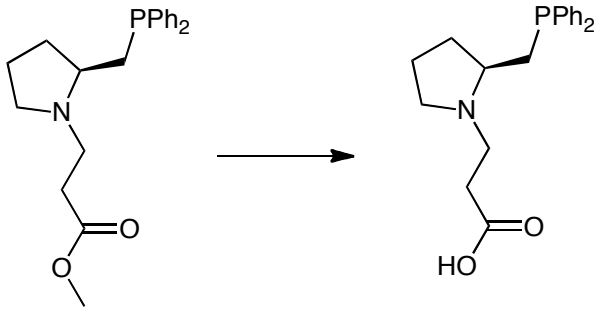
^{31}P NMR (162 MHz, $CDCl_3$) δ = -20.61 (s), 30.40 (s, P=O, 5%).

IR (diamond, ν_{MAX}, cm^{-1}) 2956, 2547 (HO st), 1720 (C=O st), 1432 (H-C-H st as).

$[\alpha]_D^{26}$=−40.0 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{20}H_{25}NO_2P$
Found: 342.1608 m/z *error [ppm]: 2.86*
Calculated: 342.1617 m/z

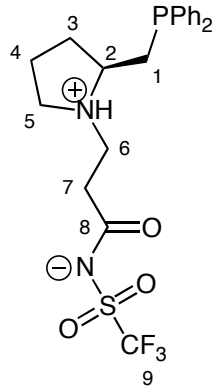
Rf (methanol : dichloromethane, [5:95]): 0.15 (blue, PMA dip)



Procedure

A solution of 34.3 mL of the 1N sodium hydroxide was added to methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}propanoate (0.50 g, 1.41 mmol) in methanol (22.85 mL, 0.062M). After stirring for 20 h at room temperature the reaction mixture was neutralized with 32% hydrochloric acid (3.5 mL). The resulting solution was lyophilized to yield. The crude product was dissolved in methanol and the insoluble salts were removed by filtration. The resultant solution was dried over magnesium sulfate, filtered and concentrated under reduced pressure to give the corresponding compound as a yellow and cloudy viscous oil (0.57 g, quantitative).

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide (196)



Appearance: white solid **Yield:** 49%

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^{1}H NMR (500 MHz, DMSO) δ = 7.55 – 7.32 (10H, m, Ar), 3.75 – 3.45 (2H, m, 5, 6-H), 3.22 (1H, s, 2-H,), 3.11 – 2.89 (3H, m, 1, 5, 6-H), 2.55 – 2.45 (2H, m, 7-H), 2.28 (1H, t, *J*=12.1, 1-H), 2.15 – 2.03 (1H, m, 3-H), 1.94 – 1.77 (2H, m, 4-H), 1.74 – 1.60 (1H, m, 3-H).

^{13}C NMR (126 MHz, DMSO) δ = 174.3 (s, 8-C), 137.3 (d, *J*=12.2, Ar), 136.2 (d, *J*=13.2, Ar), 132.7 (d, *J*=19.9, Ar), 132.4 (d, *J*=19.6, Ar), 129.2 (d, *J*=33.7, Ar), 128.8 (d, *J*=7.1, Ar), 128.6 (d, *J*=7.0, Ar), 124.1 (s, 9-CF), 121.5 (s, 9-CF), 118.9 (s, 9-CF), 116.4 (s, 9-CF), 66.1 (d, *J*=23.5, 2-CH), 52.8 (s, 5-CH_2), 49.6 (s, 6-CH_2), 34.3 (s, 7-CH_2), 30.1 (s, 3-CH_2), 28.9 (d, *J*=13.0, 1-CH_2), 21.4 (s, 4-CH_2).

^{31}P NMR (162 MHz, DMSO) δ = -21.76 (s).

^{19}F NMR (376 MHz, DMSO) δ = -77.71 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 3052, 2967 (NH st), 2192 (Ar comb), 1598 (C=O st amide), 1431 (H-C-H st as), 1176 (S-O st as), 1123 (S-O st sy).

$[\alpha]_D^{26}$=−27.7 (*c*=1.0 in dichloromethane).

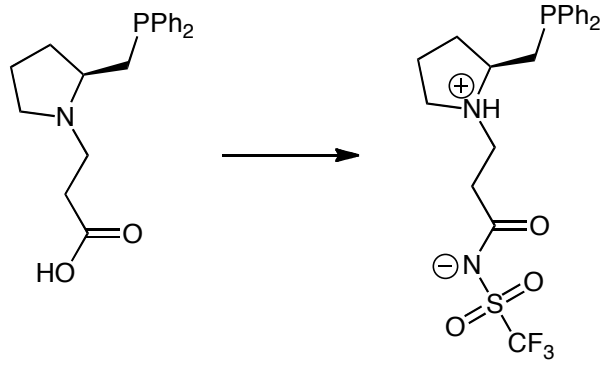
Acc. Mass (FAB): $C_{21}H_{24}F_3N_2NaO_3PS$

Found: 495.1117 m/z *error [ppm]: -5.50*

Calculated: 495.1090 m/z

X-Ray: see appendix **196** (The complex (30 mg, 0.062 mmol) was recrystallised from chloroform at room temperature).

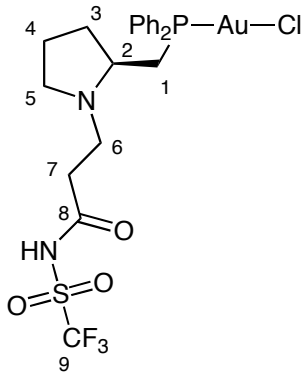
Rf (methanol : dichloromethane, [5:95]): 0.49 (blue, PMA dip)



Procedure

3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}propanoic acid (0.50 g, 1.46 mmol), triflic amine (0.218 g, 1.46 mmol) and HOBt∗H_2O (0.224 g, 1.46 mmol) were dissolved in dichloromethane (3.85 mL) and cooled to 0 °C. EDC (0.233 g, 1.50 mmol) was added and mixture was stirred for 15 min at 0 °C and then at room temperature overnight. The precipitate was filtered off and solvent was evaporated. The residue was dissolved in 20 mL of dichloromethane and washed with 1M citric acid (20 mL), saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous magnesium sulfate; concentrated under reduced pressure. Purification by column chromatography (methanol:dichloromethane, [5:95]) afforded the title compound as white solid (0.34 g, 49%).

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide gold chloride (198)



Appearance: white solid **Yield:** 94%

1H NMR (500 MHz, $CDCl_3$) δ = 7.92 (2H, dd, *J*=7.1, 13.6, Ar), 7.80 (2H, dd, *J*=7.1, 13.4, Ar), 7.59 – 7.42 (6H, m, Ar), 4.26 (1H, m, 5-H), 3.86 – 3.58 (2H, m, 6-H), 3.53 – 3.37 (2H, m, 1-H), 3.02 – 2.90 (2H, m, 5,6-H), 2.83 – 2.55 (2H, m, 7-H), 2.19 – 1.91 (3H, m, 3,4-H), 1.80 – 1.67 (1H, m, 3-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.6 (s, 8-C), 134.1 (d, *J*=14.3, Ar), 133.1 (d, *J*=13.6, Ar), 132.6 (dd, *J*=2.1, 52.4, Ar), 129.5 (dd, *J*=6.8, 12.1, Ar), 128.6 (d, *J*=63.1, Ar), 127.9 (d, *J*=61.7, Ar), 124.12(s, 9-CF), 121.5 (s, 9-CF), 119.0 (s, 9-CF), 116.4 (s, 9-CF), 67.7 (s, 2-CH), 54.6 (s, 5-CH_2), 52.3 (s, 6-CH_2), 34.5 (s, 7-CH_2), 30.4 (s, 3-CH_2), 29.1 (d, *J*=38.9, 1-CH_2), 21.9 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 26.38 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -78.34 (s).

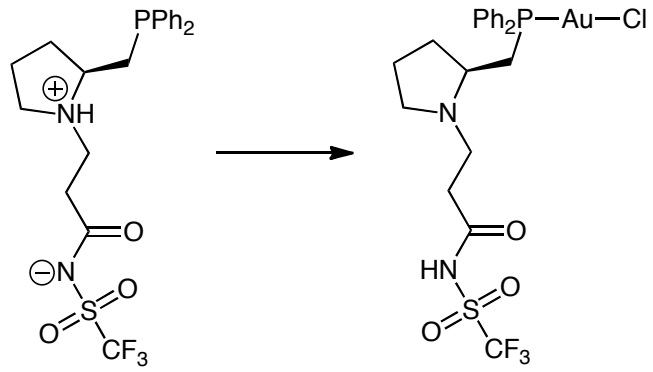
IR (diamond, ν_{MAX}, cm^{-1}) 3055 (NH st), 2191 (Ar comb), 1610 (C=O st amide), 1437 (H-C-H st as), 1173 (S-O st as), 1124 (S-O st sy).

$[\alpha]_D^{26}$=−12.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{21}H_{24}AuClF_3N_2NaO_3PS$

Found: 727.0440 m/z *error [ppm]: 0.48*

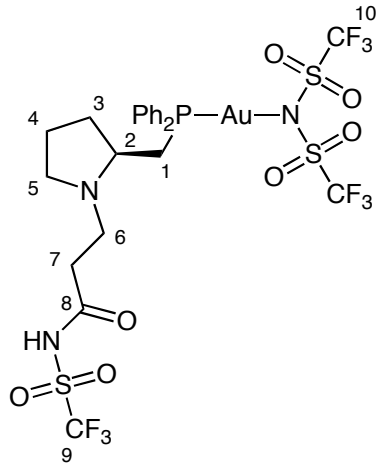
Calculated: 727.0444 m/z



Procedure

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl) ((trifluoromethyl)sulfonyl)amide (50 mg, 0.106 mmol) was dissolved in dry dichloromethane (1 mL) under an atmosphere of nitrogen. Dimethyl sulfide gold chloride (31 mg, 0.106 mmol) was added in one portion and resulting mixture was stirred for 3 h. Concentration of the reaction mixture under reduced pressure afforded the title compound as a white solid (70 mg, 94%).

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide gold bistriflic amide (199)



Appearance: white solid **Yield:** 80%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17 – 6.96 (10H, m, Ar), 4.33 -2.89 (9H, m, 1,5,6,7-H), 2.22 – 1.75 (3H, m, 3,4-H), 1.47 – 1.21 (1H, m, 3-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.8 (s, C-8), 134.9 (d, *J*=14.0, Ar), 133.8 (s, Ar), 132.2 (s, Ar), 131.7 (d, *J*=12.2, Ar), 130.0 (s, Ar), 129.6 (s, Ar), 129.4 (d, *J*=11.7, Ar), 123.4 (s, CF), 120.9 (s, CF), 118.3 (s, CF), 115.7 (s, CF), 64.4 (s, 2-CH), 52.8 (s, 5-CH_2), 44.9 (s, 6-CH_2), 29.5, 29.1 (s, 1, 3, 7-CH_2), 20.8 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 26.78 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -76.56 (s), -78.68 (s).

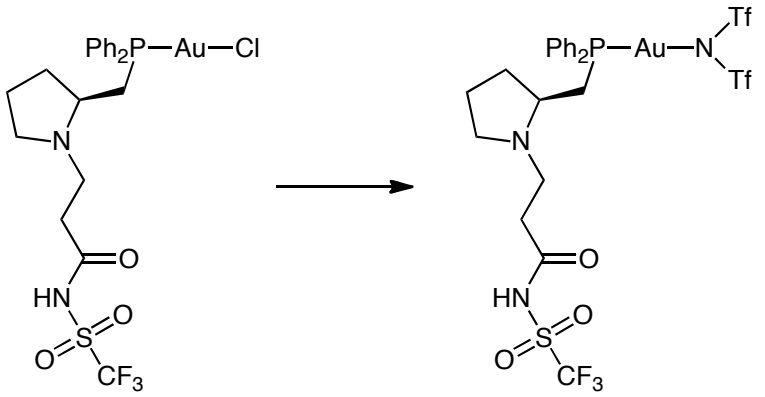
IR (diamond, ν_{MAX}, cm^{-1}) 2178 (Ar comb), 1669 (C=O st amide), 1439 (H-C-H st as), 1178 (S-O st as), 1128 (S-O st sy).

$[\alpha]_D^{26}$=−23.6 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{23}H_{24}AuF_9N_3O_7PS_3$

Found: N/A *error [ppm]: N/A*

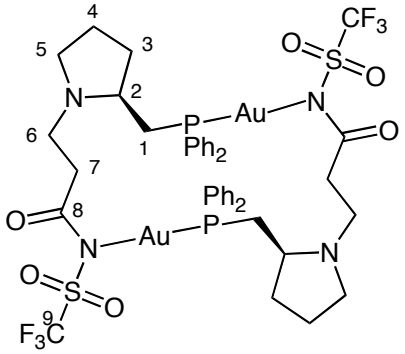
Calculated: 949.5735



Procedure

A solution of gold diphenylphosphine chloride (65.2 mg, 0.092 mmol) in dichloromethane (0.31 mL) was added premixed (5 min.) solution of bistriflic amide (26 mg, 0.092 mmol) and silver carbonate (25.5 mg, 0.092 mmol) in dry dichloromethane (2 mL) under an inert atmosphere. The resulting mixture was stirred for 2 h excluding light. The mixture was filtered through Celite and concentrated under reduced pressure to give the title compound as an off white solid (70.5 mg, 80%).

Bidentate gold(I) complex – dimer (197)



Appearance: white solid **Yield:** 98%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 – 7.37 (10H m, Ar), 3.36 – 1.23 (13H m, 1-7-H **).**

^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.6 (s, 8-C), 133.6 (s, Ar), 133.0 (s, Ar), 132.2 (s, Ar), 129.9 (s, Ar), 129.4 (s, Ar), 129.3 (s, Ar), 125.4 (s, 9-CF), 122.1 (s, 9-CF), 118.7 (s, 9-CF), 115.5 (s, 9-CF), 61.8 (s, 2-CH), 53.4 (s, 5-CH_2), 50.04 (s, 6-CH_2), 37.4 (s, 7-CH_2), 33.2 (s, 3-CH_2), 31.9 (s, 1-CH_2), 22.8 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 21.92 (s), 20.81 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2962 (NH st), 2168 (Ar comb), 1683 (C=O st amide), 1437 (H-C-H st as), 1177 (S-O st as), 1121 (S-O st sy).

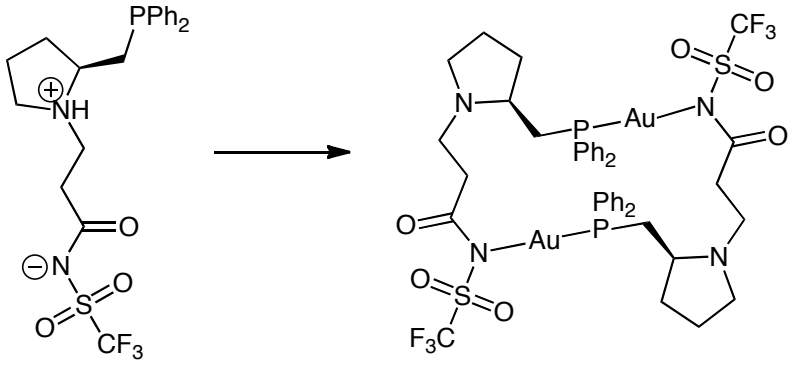
$[\alpha]_D^{24}$=−21.2 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{42}H_{47}Au_2F_6N_4O_6P_2S_2$

Found: 1337.1704 m/z *error [ppm]: -4.61*

Calculated: 1337.1704 m/z

X-Ray: available see Appendix (The complex (30 mg, 0.023 mmol) was recrystallised by slow diffusion of dichloromethane (0.2 mL) into benzene (0.3 mL) at +5 °C with slow evaporation).

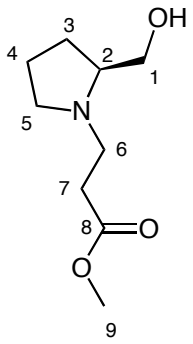


Procedure

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl) ((trifluoromethyl)sulfonyl)amide

(100 mg, 0.212 mmol) was dissolved in dry dichloromethane (2.1 mL) in a flame dried flask, under nitrogen. The dimethyl sulfide gold chloride (62 mg, 0.212 mmol) was added in one portion and mixture was stirring 15 min. The silver carbonate (58 mg, 0.212 mmol) was added in one portion and the resultant mixture stirred overnight. The reaction was filtered through Celite and concentrated under reduced pressure to give the title compound as a yellow solid (139 mg, 98%).

Methyl 3-[(2*S*)-2-(hydroxymethyl)pyrrolidin-1-yl]propanoate (192)



Appearance: colorless oil **Yield:** 72%

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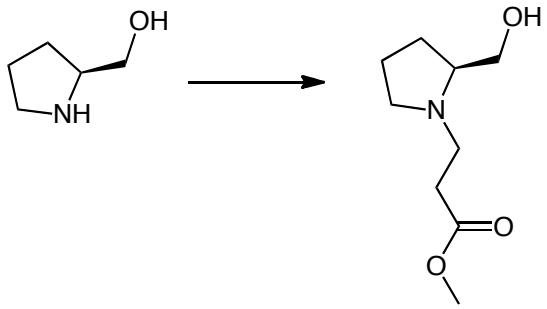
^{1}H NMR (500 MHz, $CDCl_3$) δ = 3.69 (3H, s, 9-H), 3.65 (1H, dd, *J*=3.4, 11.0, 1-H), 3.36 (1H, dd, *J*=3.2, 11.0, 1-H), 3.20 – 3.11 (2H, m, 5, 6-H), 2.80 (1H, br s, OH), 2.65 – 2.43 (4H, m, 2, 5, 7-H), 2.27 – 2.21 (1H, m, 6-H), 1.89 – 1.68 (4H, m, 3, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.16 (s, 8=C), 64.7 (s, 2-CH), 62.4 (s, 1-CH_2), 54.1 (s, 5-CH_2), 51.6 (s, 9-CH_2), 49.7 (s, 6-CH_2), 34.0 (s, 7-CH_2), 27.4 (s, 3-CH_2), 23.6 (s, 4-CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 3447, 2952, 2811 (HO st), 1733 (C=O st), 1437 (H-C-H st as), 1199 (C-O st).

$[\alpha]_D^{22}$=−53.0 (*c*=1.0 in dichloromethane).

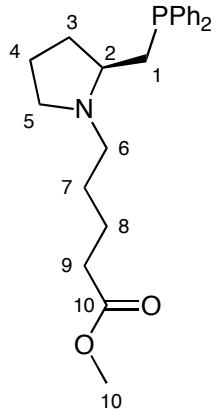
Acc. Mass (FAB): $C_9H_{17}NNaO_3$
Found: 210.1097 *error [ppm]: 1.51*
Calculated: 210.1101



Procedure

(*L*)-prolinol (185 mg, 1,82 mmol) was dissolved in dichloromethane (5.2 mL). Triethylamine (370 mg, 3.66 mmol, 0.51 mL) and methyl 3-bromopropionate (336 mg, 2.01 mmol, 022 mL) were added and the resulting mixture stirred overnight at 30 °C. The reaction was poured into water/dichloromethane (14 mL/ 14 mL). The crude residue was extracted with 20 mL of dichloromethane; the organic layer was washed with water (20 mL), brine (20 mL) and dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography ([5:95], methanol : dichloromethane) afforded the title compound as colorless oil (245.5 mg, 72%).

(*S*)-methyl 5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoate (200)



Appearance: colorless oil **Yield:** 65%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55 – 7.27 (10H, m, Ar), 3.66 (3H, s, 11-H), 3.21 (1H, s, 5-H), 2.82 (1H, m, 5-H), 2.54 (1H, dt, *J*=3.1, 13.2, 3-H), 2.40 (1H, s, 2-H), 2.33 – 2.27 (2H, m, 9-H), 2.21 – 2.04 (3H, m, 3, 6-H), 2.04 – 1.96 (1H, m, 1-H), 1.83 (1H, m, 4-H), 1.74 – 1.45 (5H, m, 4, 7, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.9 (s, 10-C), 133.09 (s, Ar), 132.94 (s, Ar), 132.62 (s, Ar), 132.47 (s, Ar), 128.82 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 62.8 (s, 2-CH), 53.6 (s, 6-CH_2), 53.5 (s, 5-CH_2), 51.5 (s, 11-CH_3), 33.8 (s, 9-CH_2), 33.2 (s, 3-CH_2), 31.6 (s, 1-CH_2), 27.6 (s, 7-CH_2), 22.9 (s, 8-CH_2), 22.1 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -20.82 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2945, 2788 (CH_3O st), 1734 (C=O st), 1433 (H-C-H st as), 1169 (C-O st as).

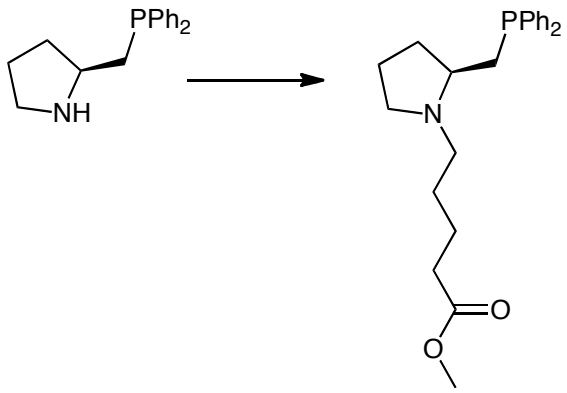
$[\alpha]_D^{24}$=−46.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{23}H_{31}NO_2P$

Found: 384.2078 *error [ppm]: 2.43*

Calculated: 384.2087

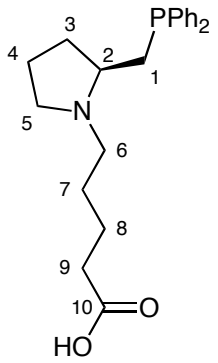
Rf (methanol : dichloromethane, [5:95]): 0.32 (blue, PMA dip)



Procedure

A solution of methyl 5-bromopentanoate (0.36 g, 1.86 mmol, 0.27 mL) in dichloromethane (1.64 mL) was added dropwise to a solution of triethylamine (0.38 g, 3.71 mmol, 0.52 mL) and (2*S*)-2-[(diphenylphosphino)methyl]pyrrolidine (0.500 g, 1.86 mmol) in dichloromethane (5.46 mL). The resultant solution was stirred at 30 °C overnight. The reaction mixture was poured into water/dichloromethane (1:1, 40 mL). The crude residue was extracted with dichloromethane (20 mL), the organic phase was washed with water (20 mL), brine (20 mL) and then dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (methanol : dichloromethane, [5:95]) afforded the title compound as a yellow cloudy viscous oil (1.57 g, 65%).

(*S*)-5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoic acid (204)



Appearance: colorless oil **Yield:** 93%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 11.94 – 11.20 (1H, br s, OH), 7.59 – 7.30 (10H, m, Ar), 3.84 (1H, s, 5-H), 3.26 (1H, s, 6-H), 3.03 – 2.56 (5H, m, 1, 2, 5, 6-H), 2.34 (2 H, t, *J*=6.7, 9-H), 2.20 (2 H, s, 3, 4-H), 2.04 (1 H, s, 3-H), 1.93 (2 H, s, 4, 7-H), 1.74 – 1.52 (3 H, m, 7, 8-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.6 (s, 10-C), 136.4 (s, Ar), 133.2 (d, *J*=14.26, Ar), 132.5 (s, Ar), 129.7 (s, Ar), 129.1 (s, Ar), 128.9 (s, Ar), 128.7 (s, Ar), 67.1 (s, 2-CH), 52.9 (s, 5, 6-CH_2), 33.1 (s, 9-CH_2), 30.6 (s, 3-CH_2), 29.8 (s, 1-CH_2), 24.4 (s, 7-CH_2), 22.0 (s, 8-CH_2), 21.7 (s, 4-CH_2).

IR (diamond, ν_{MAX}, cm^{-1}) 2945, 2546 (HO st), 1720 (C=O st), 1432 (H-C-H st as), 1169 (C-O st as).

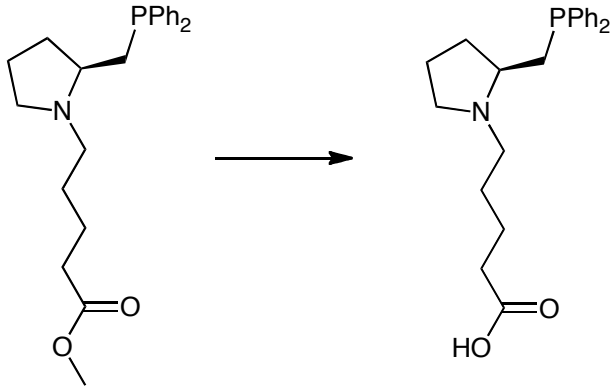
$[\alpha]_D^{24}$=−44.1 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{22}H_{29}NO_2P$

Found: 370.1921 *error [ppm]: 2.57*

Calculated: 370.1930

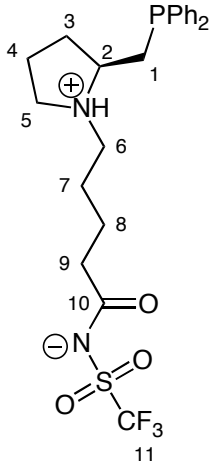
Rf (methanol : dichloromethane, [5:95]): 0.17 (blue, PMA dip)



Procedure

A solution of 27.5 mL of the 1N sodium hydroxide was added to methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}pentanoate (0.41 g, 1.11 mmol) in methanol (18.5 mL, 0.062M). After stirring for 20 h at room temperature the reaction mixture was neutralized with 32% hydrochloric acid (2.8 mL). The resulting solution was lyophilized to yield. The crude product was dissolved in methanol and the insoluble salts were removed by filtration. The resultant solution was dried over magnesium sulfate, filtered and concentrated under reduced pressure to give the corresponding compound as a yellow and cloudy viscous oil (0.38 g, 93%).

(5-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)pentanoyl)((trifluoromethyl)sulfonyl)amide (206)



Appearance: white solid **Yield:** 66%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56 – 7.30 (10H, m, Ar), 3.98 (1H, s, 5-H), 3.40 (1H, s, 6-H), 2.95 (1 H, s, 2-H), 2.82 (2 H, m, 1, 5-H), 2.63 – 2.38 (4 H, m, 1, 6, 9-H), 2.29 – 2.16 (2 H, m, 3, 4-H), 2.08 – 1.86 (2 H, m, 3, 4-H), 1.79 (1 H, s, 7-H), 1.71 – 1.52 (3 H, m, 7, 8H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 181.0 (s, 10-C), 136.7 (d, *J*=11.4, Ar), 136.4 (d, *J*=10.9, Ar), 133.1 (d, *J*=20.1, Ar), 132.4 (d, *J*=19.1, Ar), 129.7 (s, Ar), 129.1 (s, Ar), 129.0 (d, *J*=7.2, Ar), 128.7 (d, *J*=6.6, Ar), 124.2 (s, 10-CF), 121.7 (s, 10-CF), 119.1 (s, 10-CF), 68.4 (d, *J*=23.9, 2-CH), 54.8 (s, 6-CH_2), 53.8 (s, 5-CH_2), 37.5 (s, 9-CH_2), 30.6 (d, *J*=7.1, 3-CH_2), 29.8 (d, *J*=15.1, 1-CH_2), 24.7 (s, 7-CH_2), 22.6 (s, 8-CH_2), 21.7 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -20.38 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2962 (NH st), 2192 (Ar comb), 1602 (C=O st amide), 1431 (H-C-H st as), 1168 (S-O st as), 1126 (S-O st sy).

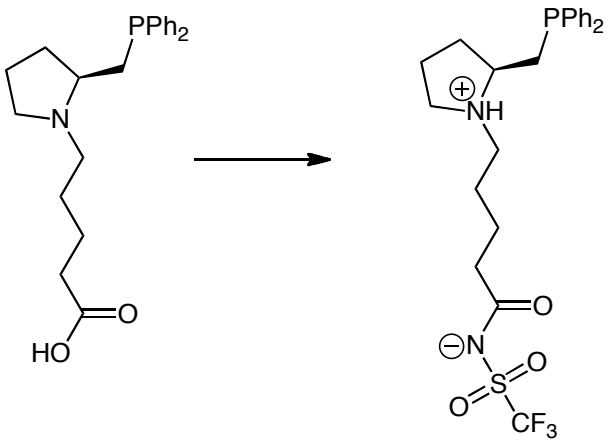
$[\alpha]_D^{24}$=−21.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{23}H_{28}F_3N_2NaO_3PS$

Calculated: 523.1403 *error [ppm]: 2.11*

Found: 523.1392

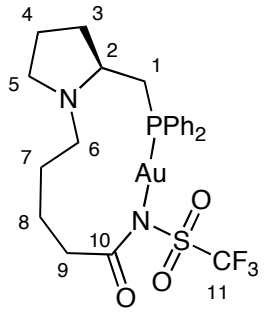
Rf (methanol : dichloromethane, [5:95]): 0.31 (blue, PMA dip)



Procedure

(*S*)-5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoic acid (0.300 g, 0.81 mmol), triflic amine (0.121 g, 0.81 mmol) and HOBt•H_2O (0.125 g, 0.14 mmol) were dissolved in dichloromethane (2.15 mL) and cooled to 0 °C. EDC (0.140 g, 0.83 mmol) was added and mixture was stirred for 15 min at 0 °C and then at room temperature overnight. The precipitate was filtered off and solvent was evaporated. The residue was dissolved in 15 mL of dichloromethane and washed with 1M citric acid (15 mL), saturated sodium bicarbonate (15 mL), brine (15 mL) and dried over anhydrous magnesium sulfate; concentrated under reduced pressure. Purification by column chromatography (methanol:dichloromethane, [5:95]) afforded the title compound as white solid (0.268 g, 66%).

Bidentate gold(I) complex – monomer (207)



Appearance: white solid **Yield:** quantitative

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83 – 7.69 (4H, m, Ar), 7.57 – 7.45 (6H, m, Ar), 3.12 – 3.04 (1H, m, 6-H), 2.97 – 2.63 (5H, m, 2, 3, 5, 9-H), 2.57 – 2.47 (1H, m, 9-H), 2.33 – 2.20 (2H, m, 6- 8-H), 2.19 – 2.10 (1H, m, 5-H), 1.90 – 1.45 (6H, m, 1, 4, 8, 7-H), 1.35 – 1.24 (1H, m, 1-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.8 (s, 10-C), 133.1 (d, *J*=12.9, Ar), 133.5 (d, *J*=13.9, Ar), 132.1 (d, *J*=22.7, Ar), 129.5 (s, Ar), 129.4 (s, Ar), 129.4 (s, Ar), 122.0 (s, 11-CF), 61.6 (s, 2-CH), 53.3 (s, 6-CH_2), 51.6 (s, 5-CH_2), 40.2 (s, 9-CH_2), 32.3 (d, *J*=40.9, 3-CH_2), 31.3 (s, 1-CH_2), 26.4 (s, 7-CH_2), 23.9 (s, 8-CH_2), 22.3 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 16.41 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2925, 2798 (NH st), 2168 (Ar comb), 1694 (C=O st amide), 1436 (H-C-H st as), 1176 (S-O st as), 1123 (S-O st sy).

$[\alpha]_D^{24}$=−22.3 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{23}H_{28}AuF_3N_2NaO_3PS$

Found: 719.0962 *error [ppm]: 0.52*

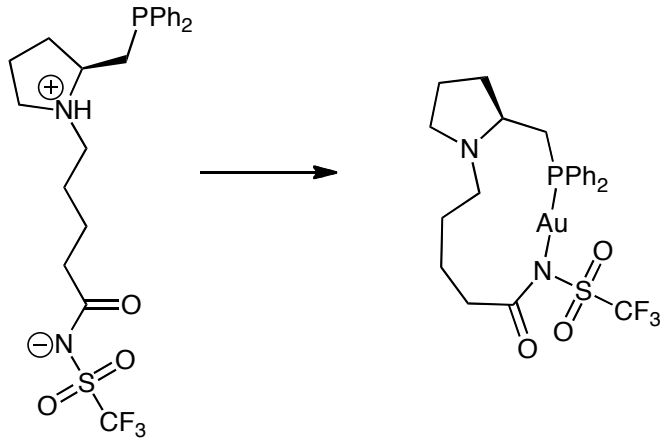
Calculated: 719.0966

Acc. Mass (FAB): $C_{46}H_{54}Au_2F_6N_4NaO_6P_2S_2$

Found: 1415.2089 *error [ppm]: -0.12*

Calculated: 1415.2087

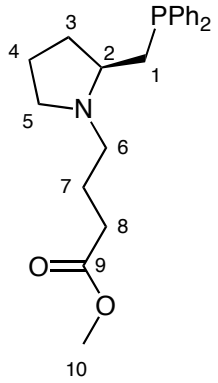
X-Ray: see appendix **207** (The complex (30 mg, 0.021 mmol) was recrystallised by slow diffusion of dichloromethane (0.1 mL) into n-heptane (0.4 mL) at +5 °C).



Procedure

The (5-((2*S*)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)pentanoyl) ((trifluoromethyl)sulfonyl)amide (100 mg, 0.199 mmol) was dissolved in dry dichloromethane (2.0 mL) in a flame dried flask, under nitrogen. The dimethyl sulfide gold chloride (58.9 mg, 0.199 mmol) was added in one portion and mixture was stirring 15 min. The silver carbonate (55.1 mg, 0.199 mmol) was added in one portion and the resultant mixture stirred overnight. The reaction was filtered through Celite and concentrated under reduced pressure to give the title compound as a yellow solid (138.7 mg, quantitative).

(*S*)-methyl 4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)butanoate (202)



Appearance: colorless oil **Yield:** 47%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 – 7.40 (4H, m, Ar), 7.38 – 7.28 (6H, m, Ar), 3.66 (3H, d, *J*=1.3, 11-H), 3.19 (1H, s, 5-H), 2.80 (1 H, m, 6-H), 2.51 (1 H, d, *J*=13.1, 1-H), 2.46 – 2.22 (3H, m, 2, 8-H), 2.14 (3H, s, 1, 5, 6-H), 2.03 – 1.94 (1H, m, 3-H), 1.86 – 1.57 (5H, m, 3, 4, 7-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.8 (s, 10-C), 139.2 (s, Ar), 138.4 (s, Ar), 133.0 (d, *J*=19.5, Ar), 132.6 (d, *J*=18.7, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 62.5 (s, 2-CH), 53.4 (s, 5-CH_2), 53.1 (s, 6-CH_2), 51.4 (s, 10-CH_3), 33.5 (s, 1-CH_2), 31.9 (s, 8-CH_2), 31.7 (d, *J*=7.4, 3-CH_2), 23.6 (s, 7-CH_2), 22.2 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = -21.02 (s).

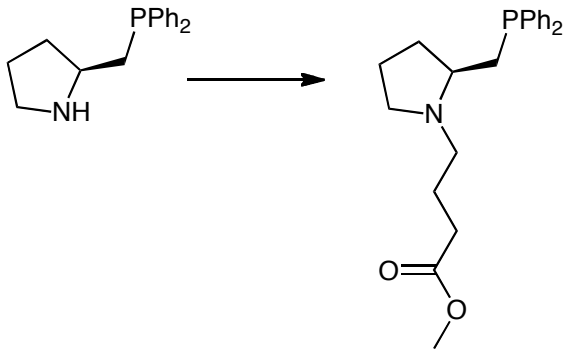
IR (diamond, ν_{MAX}, cm^{-1}) 2949, 2791 (CH_3O st), 1733 (C=O st), 1433 (H-C-H st as), 1170 (C-O st as).

Acc. Mass (FAB): $C_{22}H_{29}NO_2P$

Found: 370.1913 *error [ppm]: 4.76*

Calculated: 370.1930

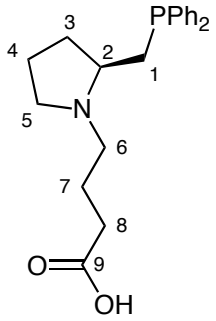
Rf (methanol : dichloromethane, [5:95]): 0.86 (blue, PMA dip)



Procedure

A solution of methyl 5-bromobutanoate (0.273 g, 1.51 mmol) in dichloromethane (1.32 mL) was added dropwise to a solution of triethylamine (0.304 g, 3.01 mmol, 0.42 mL) and (2*S*)-2-[(diphenylphosphino)methyl]pyrrolidine (0.405 g, 1.51 mmol) in dichloromethane (3.1 mL). The resultant solution was stirred at 30 °C overnight. The reaction mixture was poured into water/dichloromethane (1:1, 32 mL). The crude residue was extracted with dichloromethane (16 mL), the organic phase was washed with water (16 mL), brine (16 mL) and then dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (methanol : dichloromethane, [5:95]) afforded the title compound as a colorless viscous oil (0.264 g, 47%).

(*S*)-4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)butanoic acid (203)



Appearance: colorless oil **Yield:** quantitative

---

^{1}H NMR (500 MHz, CD_3OD) δ = 7.58 – 7.45 (4H, m, Ar), 7.44 – 7.35 (5H, m, Ar), 3.70 – 3.60 (1H, m, 5-H), 3.40 – 3.32 (1H, m, 6-H), 3.25 – 3.14 (1H, m, 2-H), 3.13 – 3.02 (1H, m, 5-H), 3.00 – 2.90 (1H, m, 6-H), 2.84 (1H, dd, *J*=3.4, 13.3, 1-H), 2.48 – 2.35 (3H, m, 1, 8-H), 2.32 – 2.23 (1H, m, 3-H), 2.10 – 1.80 (5H, m, 3, 4, 7-H).

^{13}C NMR (126 MHz, CD_3OD) δ = 181.3 (s, 9-C), 138.8 (d, *J*=11.5, Ar), 137.9 (d, *J*=12.4, Ar), 134.3 (d, *J*=20.2, Ar), 133.8 (d, *J*=19.5, Ar), 130.8 (s, Ar), 130.4 (s, Ar) 130.1 (d, *J*= 7.3, Ar), 129.9 (d, *J*=7.0, Ar), 67.4 (d, *J*=21.9, 2-CH), 55.2 (s, 6-CH_2), 54.4 (s, 5-CH_2), 36.2 (s, 8-CH_2), 32.0 (d, *J*=7.8, 3-CH_2), 31.5 (d, *J*=15.8, 1-CH_2), 23.3 (s, 7-CH_2), 22.9 (s, 4-CH_2).

^{31}P NMR (162 MHz, CD_3OD) δ = -21.13 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 3307, 2541 (HO st), 1586 (C=O st), 1432 (H-C-H st as) 1154 (C-O st as).

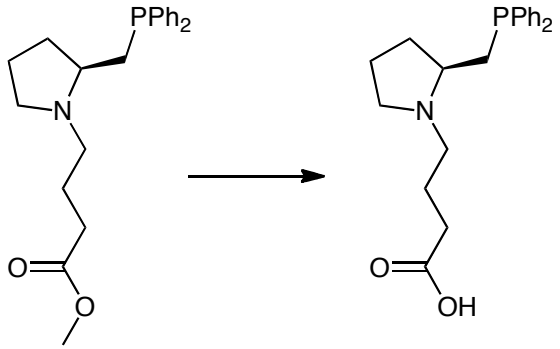
$[\alpha]_D^{23}$=−13.9 (*c*=1.0 in methanol).

Acc. Mass (FAB): $C_{22}H_{29}NO_2P$

Found: 356.1768 *error [ppm]: 1.76*

Calculated: 356.1774

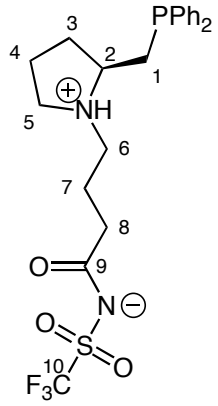
Rf (methanol : dichloromethane, [5:95]): 0.16 (blue, PMA dip)



Procedure

A solution of 15.7 mL of the 1N sodium hydroxide was added to methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}butanoate (0.237 g, 0.64 mmol) in methanol (10.4 mL, 0.062M). After stirring for 20 h at room temperature the reaction mixture was neutralized with 32% hydrochloric acid (1.7 mL). The resulting solution was lyophilized to yield. The crude product was dissolved in methanol and the insoluble salts were removed by filtration. The resultant solution was dried over magnesium sulfate, filtered and concentrated under reduced pressure to give the corresponding compound as a yellow and cloudy viscous oil (0.228 g, quantitative).

(4-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)butanoyl)((trifluoromethyl)sulfonyl)amide (205)



Appearance: white solid **Yield:** 46%

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^{1}H NMR (500 MHz, DMSO) δ = 7.61 – 7.35 (10H, m, Ar), 3.58 (1H, s, 5-H), 3.45 – 3.37 (1H, m, 6-H), 3.20 (1H, s, 2-H), 3.09 – 3.02 (1H, m, 5-H), 2.99 – 2.84 (2H, m, 1, 6-H), 2.31 – 2.09 (4H, m, 1, 3, 8-H), 1.97 – 1.60 (5H, m, 3, 4, 7-H).

^{13}C NMR (126 MHz, DMSO) δ = 176.6 (s, 9-C), 137.3 (d, *J*=12.1, Ar), 136.0 (d, *J*=13.1, Ar), 132.7 (d, *J*=20.0, Ar), 132.4 (d, *J*=19.5, Ar), 129.4 (s, Ar), 129.1 (s, Ar), 128.8 (d, *J*=7.2, Ar), 128.6 (d, *J*=6.9, Ar), 124.3 (s, 10-CF), 121.7 (s, 10-CF), 119.1 (s, 10-CF), 116.5 (s, 10-CF), 65.7 (d, *J*=21.9, 2-CH), 52.6 (s, 5-CH_2), 52.3 (s, 6-CH_2), 36.0 (s, 8-CH_2), 30.0 (d, *J*=8.3, 3-CH_2), 28.7 (d, *J*=14.3, 1-CH_2), 21.5 (s, 7-CH_2), 21.2 (s, 4-CH_2).

^{31}P NMR (162 MHz, DMSO) δ = -25.01 (1s).

IR (diamond, ν_{MAX}, cm^{-1}) 2967, 2554 (NH st), 2192 (Ar comb), 1645 (C=O st amide), 1434 (H-C-H st as), 1158 (S-O st as), 1134 (S-O st sy).

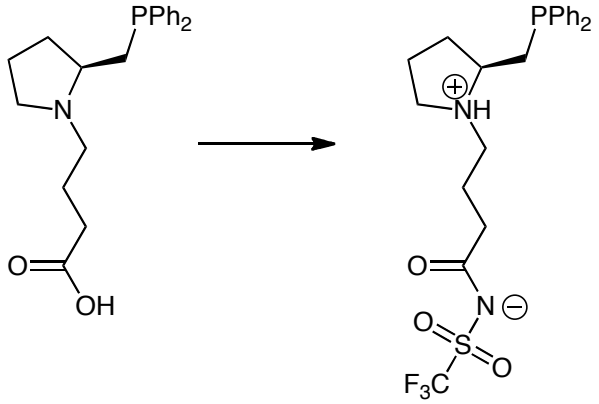
$[\alpha]_D^{22}$=−5.6 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{22}H_{26}F_3N_2NaO_3PS$

Calculated: 509.1246 *error [ppm]: 0.31*

Found: 509.1244

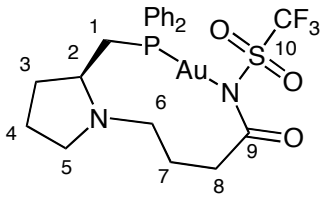
Rf (methanol : dichloromethane, [5:95]): 0.53 (blue, PMA dip)



Procedure

(*S*)-5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)butanoic acid (0.233 g, 0.65 mmol), triflic amine (0.098 g, 0.65 mmol) and HOBt•H_2O (0.100 g, 0.65 mmol) were dissolved in dichloromethane (1.72 mL) and cooled to 0 °C. EDC (0.104 g, 0.67 mmol) was added and mixture was stirred for 15 min at 0 °C and then at room temperature overnight. The precipitate was filtered off and solvent was evaporated. The residue was dissolved in 10 mL of dichloromethane and washed with 1M citric acid (10 mL), saturated sodium bicarbonate (10 mL), brine (10 mL) and dried over anhydrous magnesium sulfate; concentrated under reduced pressure. Purification by column chromatography (methanol:dichloromethane, [5:95]) afforded the title compound as white solid (0.145 g, 46%).

Bidentate Gold(I) complex – monomer and dimer (208/209)



Appearance: yellow solid **Yield:** quantitative w/w

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89 – 7.33 (10H m, Ar), 3.29 – 1.52 (15H m, 1-8-H **).**

^{13}C NMR (126 MHz, $CDCl_3$) δ = 177.6 (s, 9-C), 133.5 (s, Ar), 133.0 (s, Ar), 132.2 (s, Ar), 132.0 (s, Ar), 131.0 (s, Ar), 129.9 (s, Ar), 129.4 (s, Ar), 129.4 (s, Ar), 129.0 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 121.9 (s, 10-CF), 119.3 (s, 10-CF), 116.6 (s, 10-CF), 62.1 (s, 2-CH), 53.6 (s, 5-CH_2), 52.9(s, 6-CH_2), 33.7 (s, 1-CH_2), 33.4 (s, 8-CH_2), 32.0 (s, 3-CH_2), 24.0 (s, 7-CH_2), 22.7 (s, 4-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 23.06 (s), 21.55 (br, s), 19.68 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2935 (NH st), 2168 (Ar comb), 1688 (C=O st amide), 1436 (H-C-H st as), 1177 (S-O st as), 1121 (S-O st sy).

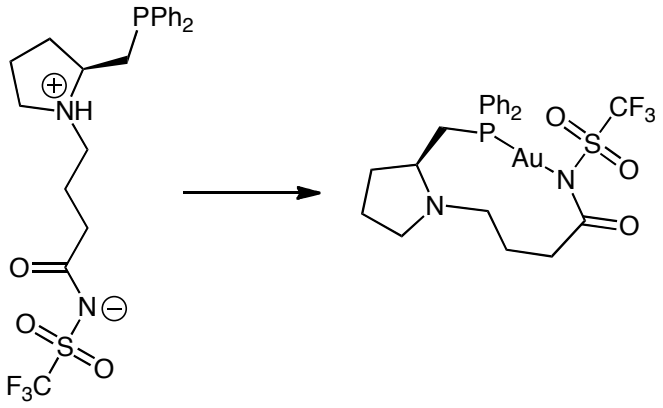
$[\alpha]_D^{20}$=-37.7 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{22}H_{26}AuF_3N_2O_3PS$
Found: 683.1014 *error [ppm]: -1.50*
Calculated: 683.1014

Acc. Mass (FAB): $C_{44}H_{51}Au_2F_6N_4O_6P_2S_2$

Found: 1365.1874 *error [ppm]: 5.91*

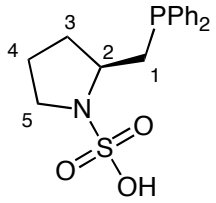
Calculated: 1365.1955



Procedure

The (4-((2*S*)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)butanoyl) ((trifluoromethyl)sulfonyl) amide (100 mg, 0.21 mmol) was dissolved in dry dichloromethane (2.1 mL) in a flame dried flask, under nitrogen. The dimethyl sulfide gold chloride (60.5 mg, 0.21 mmol) was added in one portion and mixture was stirring 15 min. The silver carbonate (56.7 mg, 0.21 mmol) was added in one portion and the resultant mixture stirred overnight. The reaction was filtered through Celite and concentrated under reduced pressure to afford the title compound as a yellow solid (122 mg, quantitative w/w (monomer or dimer)).

(*S*)-2-((diphenylphosphino)methyl)pyrrolidine-1-sulfonic acid (180)



Appearance: white solid **Yield:** 91%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 – 6.95 (10H, m, Ar), 3.76 (1H, s, 2-H), 3.32 – 2.80 (3H, m, 1, 5-H), 2.03 (1H, s, 1-H), 1.77 (1H, s, 3-H), 1.52 (3H, s, 3, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.1 (s, Ar), 139.0 (s, Ar), 132.8 (s, Ar), 132.6 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 128.3 (s, Ar), 58.8 (d, *J*=21.0, 2-CH), 50.2 (s, 5-CH_2), 35.6 (s, 1-CH_2), 32.0 (s, 3-CH_2), 24.3 (s, 4-CH_2).

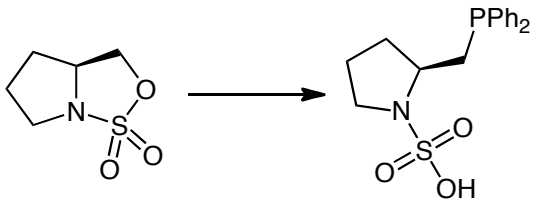
^{31}P NMR (243 MHz, $CDCl_3$) δ = -21.26 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 1433 (H-C-H st as), 1174 (-SO_3^- st as), 1041 (-SO_3^- st sy).

$[\alpha]_D^{22}$=−50.4 (*c*=1.0 in dichloromethane).

Acc. Mass (FAB): $C_{17}H_{20}NaNO_3PS$
Found: 372.0803 m/z *error [ppm]: -2.42*
Calculated: 372.0794 m/z

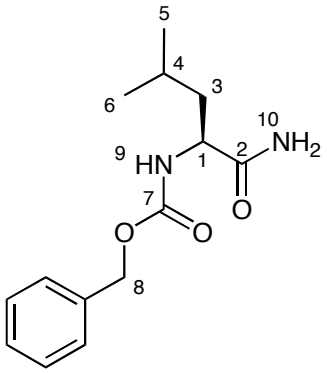
Rf (methanol : dichloromethane, [10:90]): 0.57 (blue, PMA dip)



Procedure

(*S*)-hexahydropyrrolo[1,2-*b*]isothiazole 1,1-dioxide (0.850 g, 5.21 mmol) was added to a solution of diphenylphosphinelithium (5.21 mmol, C=0.42M) in dry tetrahydrofuran (12.4 mL). The reaction was stirred 3h and quench with 8 mL of water. The crude residue was extracted with dichloromethane (3x10 mL). The organic layers were combined and concentrated under reduced pressure. Purification by column chromatography ([10:90], methanol : dichloromethane) afforded the title compound as white solid (1.648 g, 91%).

(*S*)-benzyl (1-amino-4-methyl-1-oxopentan-2-yl)carbamate (146)



Appearance: viscous oil **Yield:** 82%

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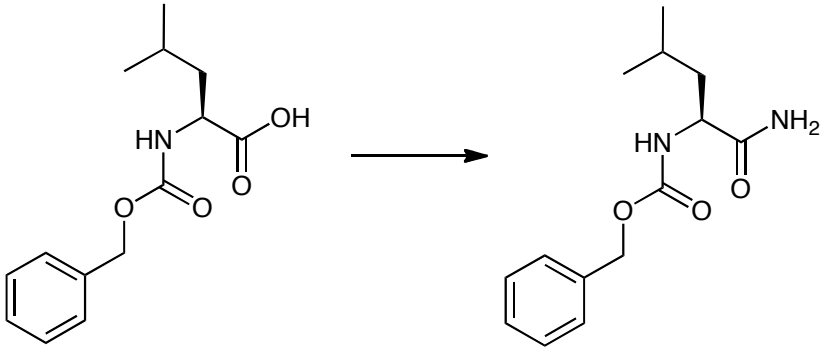
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 – 7.28 (5H, m, Ar), 6.20 (1H, s, 10-NH), 5.70 (1H, s, 10-NH), 5.33 (1H, s, 1-H), 5.10 (2 H, s, 8-H), 4.22 (1H, s, 9-NH), 1.73 – 1.63 (2 H, m, 3, 4-H), 1.52 (1 H, t, *J*=8.7, 3-H), 0.94 (6 H, d, *J*=6.1, 5, 6-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.8 (s, 2-C), 156.3 (s, 7-C), 136.1 (s, Ar), 128.5 (s, Ar), 128.2 (s, Ar), 128.0 (s, Ar), 67.1 (s, 1-CH), 53.1 (s, 8-CH_2), 41.3 (s, 3-CH_2), 24.7 (s, 4-CH), 22.9, 21.9 (s, 5, 6-CH_3).

Acc. Mass (FAB): $C_{14}H_{20}NaN_2O_3$
Found: 287.1368 m/z error [ppm]: -0.79
Calculated: 287.1366 m/z

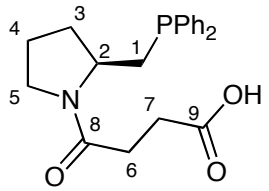
Rf (methanol : dichloromethane, [10:90]): 0.43 (blue, PMA dip)



Procedure

Methyl chloroformate (37 mg, 0.37 mmol) was added dropwise to the solution of (*S*)-2-(((benzyloxy)carbonyl)amino)-4-methylpentanoic acid (100 mg, 0.37 mmol) and triethylamine (38 mg, 0.37 mmol) in a mixture of dichloromethane/dioxane (1.88 mL/2.26 mL) at -5 °C. The reaction mixture was stirred for 30 min. at -5 °C. Aqueous ammonia (0.11 mL) was added and the reaction stirred for 4h at room temperature. The reaction was poured into 3 mL of dichloromethane and washed with 0.5 N hydrochloric acid (3x1.5 mL). The organic layers were combined and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as viscous oil (82 mg, 82%).

(*S*)-4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-4-oxobutanoic acid (182)



Appearance: white solid **Yield:** 79%

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^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.59 – 7.27 (10H, m, Ar), 4.33 – 4.25 (0.68H, m, 2-H), 3.79 (0.23H, m, 2'-H), 3.52 – 3.45 (0.55H, m, 5'-H), 3.43 – 3.34 (1.45H, m, 5-H), 2.81 – 2.75 (1H, m, 1-H), 2.68 – 2.42 (3H, m, 6, 7-H), 2.36 – 2.26 (1H, m, 6, 7-H), 2.23 – 2.05 (3H, m, 1, 3, 4), 2.04 – 1.86 (2H, m, 3, 4-H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.6 (s, 9'-C), 175.5 (s, 9-C), 170.9 (s, 8-C), 170.8 (s, 8'-C), 138.8 (d, *J*=12.0, Ar), 137.2 (d, *J*=11.8, Ar), 133.6 (d, *J*=20.2, Ar), 132.9 (s, Ar), 132.8 (s, Ar), 132.8 (s, Ar), 132.7 (s, Ar), 132.2 (d, *J*=18.2, Ar), 129.7 (s, Ar), 128.8(s, Ar), 128.8(s, Ar), 128.8(s, Ar), 128.7 (s, Ar), 128.7 (s, Ar), 128.6 (s, Ar), 128.5 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 55.9 (d, *J*=18.5, 2-CH), 55.7 (s, 2'-CH), 47.3 (s, 5-CH_2), 45.9 (s, 5'-CH_2), 34.7 (d, *J*=16.0, 1'-CH_2), 32.0 (d, *J*=14.6, 1-CH_2), 31.3 (d, *J*=6.9, 3'-CH_2), 30.0 (d, *J*=8.9, 3-CH_2), 29.8 (s, 6'-CH_2), 29.7 (s, 6-CH_2), 29.6 (s, 7-CH_2), 28.6 (s, 7'-CH_2), 24.1 (s, 4-CH_2), 21.9 (s, 4'-CH_2).

^{31}P NMR (162 MHz, $CDCl_3$) δ = 21.96 (s), 22.90 (s).

IR (diamond, ν_{MAX}, cm^{-1}) 2965 (HO st), 2188 (Ar comb), 1720 (C=O st acid), 1596 (C=O st amid) 1432 (H-C-H st as) 1166 (C-O st as).

$[\alpha]_D^{24}$=−63.2 (*c*=1.0 in dichloromethane).

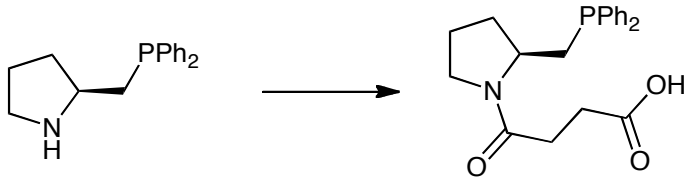
Acc. Mass (FAB): $C_{21}H_{24}NaNO_3P$

Found: 392.1396 m/z error [ppm]: -2.50

Calculated: 392.1386 m/z

X-Ray: available see Appendix (The complex (30 mg, 0.081 mmol) was recrystallised from benzene (0.5 mL) at room temperature).

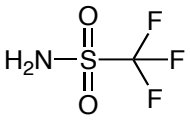
Rf (methanol : dichloromethane, [5:95]): 0.71 (blue, PMA dip)



Procedure

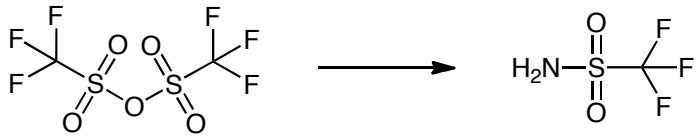
(*L*)-prolinol (0.532 g, 1.98 mmol) was dissolved in dichloromethane (19.8 mL, C = 0.1M). Triethylamine (0.300 g, 2.97 mmol, 0.42 mL) was added to the solution and stirred for 10 minutes. 4-dimethylamino pyridine (24 mg, 0.178 mmol) and succinic anhydride (0.198 g, 1.98 mmol) were added and the reaction stirred for a further 2 days at room temperature. The reaction mixture was then shaken with 3 x 25 mL portions of hydrochloric acid (2M, 3 x 25 mL), the aqueous washings were subsequently extracted with dichloromethane (3 x 50 mL). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography ([5:95], methanol : dichloromethane) afforded the title compound as white solid (0.574 g, 79%).

Trifluoromethanesulfonamide (149)



Appearance: white solid **Yield:** 89%

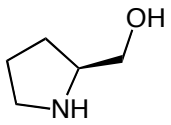
All data is identical to that reported.[102]



Procedure

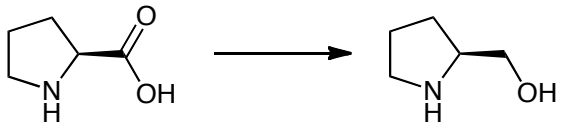
Triflic anyhydride (10.000 g, 35.45 mmol, 6 mL) was added to a round bottomed flask containing aqueous ammonia (150 mL, 35%). The solution was stirred between 0 °C and 5 °C for 16 hours. The reaction mixture was then acidified to pH 2 using conc. hydrochloric acid at 0 °C. The acidified reaction mixture was then extracted with diethyl ether (3x50 mL), the organic layers were combined and dried over magnesium sulfate and then filtered. The filtrate was concentrated under reduced pressure to yield a pale yellow solid. This was then sublimed at 140 °C/2mmHg to yield the title compound as a white solid (4.020 g, 76 %).

(*L*)-prolinol (168)



Appearance: colorless oil **Yield:** 82%

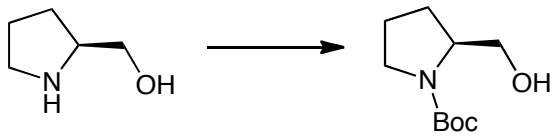
All data is identical to that reported.[117] ((*S*)-proline)



Procedure

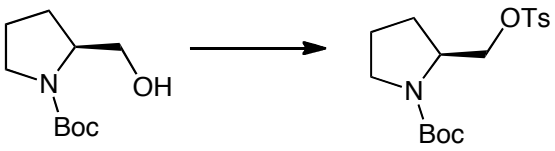
(*L*)-proline (8.000 g, 69.5 mmol) was added to a stirred solution of lithium aluminium hydride (10.548 g, 278.0 mmol) in dry tetrahydrofuran (139 mL) at 0°C. The solution was allowed to gradually warm to ambient temperature overnight and stirred for a further 12h. The reaction mixture was cooled to 0°C and an equal volume of diethyl ether added. The reaction was quenched with saturated sodium sulfate solution. The solution was filtered and the solvent removed under reduced pressure. Purification by distillation (74-76 °C/ 2 mmHg) afforded the title compound as colorless oil (5.782 g, 82%).

(*L*)-(-)-1-Boc-2-pyrrolidinemethanol (169)



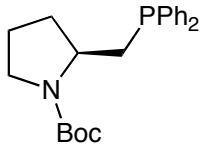
All data is identical to that reported.[118]

(*L*)-tert-butyl 2-((tosyloxy)methyl)pyrrolidine-1-carboxylate (170)



All data is identical to that reported.[119]

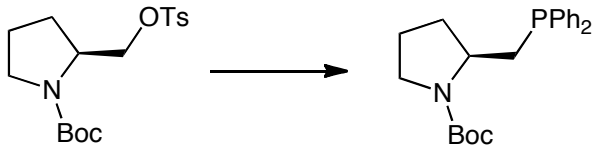
(*L*)-*tert*-butyl 2-((diphenylphosphino)methyl)pyrrolidine-1-carboxylate (172)



Appearance: yellow oil **Yield:** 60%

All data is identical to that reported.[116]

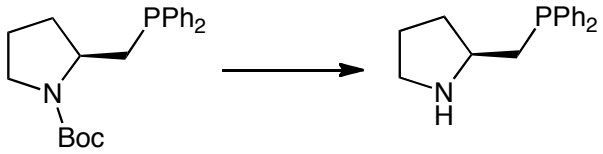
Rf (methanol : dichloromethane, [5:95]): 0.55 (blue, PMA dip)



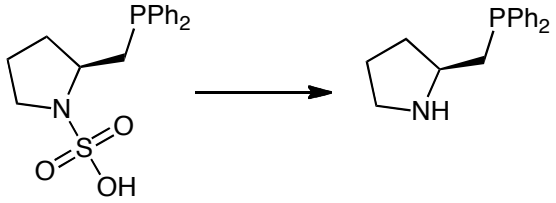
Procedure

Lithium metal (0.132 g, 19.07 mmol) was added to the solution of triphenylphosphine (2.500 g, 9.53 mmol) in dry tetrahydrofurane (20 mL) under argon and stirred overnight or until no metal was visible. A solution of (*L*)-tert-butyl 2-((tosyloxy)methyl)pyrrolidine-1-carboxylate (2.744 g, 7.72 mmol) in 10 mL of dry tetrahydrofurane was added and stirred at room temperature overnight. The reaction was quenched with 10 mL of methanol. The solvent was concentrated under reduced pressure and the residue dissolved in dichloromethane and filtered. Purification by column chromatography ([5:95], ethyl acetate : dichloromethane) afforded the title compound as yellow oil (1.708 g, 60%).

(*L*)-(-).2-[(Diphenylphosphino)methyl]pyrrolidine (173)



All data is identical to that reported.[116]



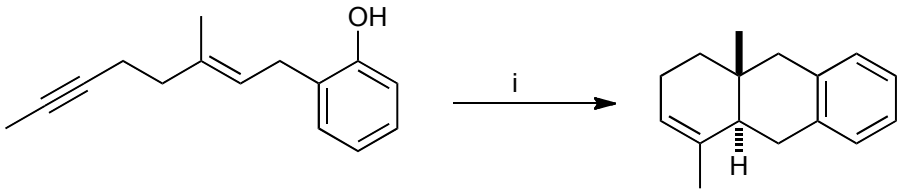
All data is identical to that reported.[116]

Procedure

Deoxygenated 32% HCl (2 mL) was added to a round bottomed flask containing (*S*)-2-((diphenylphosphino)methyl)pyrrolidine-1-sulfonic acid (100 mg, 0.30 mmol) under nitrogen and stirred for 16 h at 85°C. After cooling, the reaction was neutralized by a solution of potassium hydroxide to pH=12 and extracted with dichloromethane (3x7 mL). The reaction was concentrated under reduced pressure to give the title compound as yellow oil (53 mg, 65%).

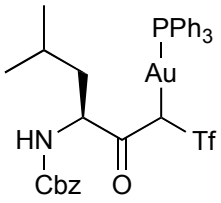
4.5 General Procedures for Reactions with Catalysts

5,8a-dimethyl-7,8,8a,9,10,10a-hexahydroanthracen-1-ol (135)



Reagents. (i) catalyst, solvent (see table below).

The starting material was prepared following Michelet procedure. All data is identical to that reported.[46]



Entry	Mol%	Solvent	Time	Yield [%]	$[\alpha]_D$
1	27	CH_2Cl_2	16h	76	0
2	5	CH_2Cl_2	5 Days	75	0
3	5	CH_2Cl_2[a]	5 Days	78	0
4	5	Benzene	5Days	63	0

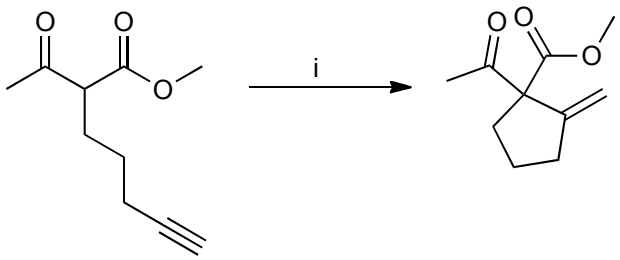
[a]- laboratory reagent grate

Procedure

(*E*)-2-(3-methyloct-2-en-6-yn-1-yl)phenol (50 mg, 0,24 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.48 ml, 0.5M) was added and the mixture stirred for around 2 minutes. The catalyst was added and the reaction mixture stirred for the appropriate time at room temperature.

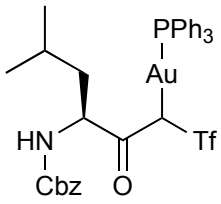
The solvent was concentrated under reduced pressure. Purification by column chromatography ([99:1], cyclohexane : ethyl acetate) afforded the title compound as light yellow oil.

Methyl 1-acetyl-2-methylenecyclopentanecarboxylate (17)



Reagents. (i) catalyst, solvent (see table below).

The starting material was prepared following Fournet procedure.[105] All data is identical to that reported.[35]

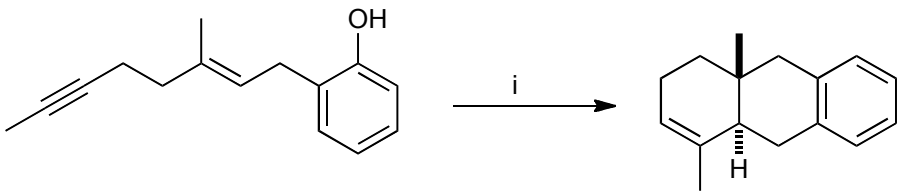


Entry	Mol%	Solvent	Time	T [C°]	Yield [%]	$[\alpha]_D$
1	5	CH_2Cl_2	5 Days	RT	95	0

Procedure

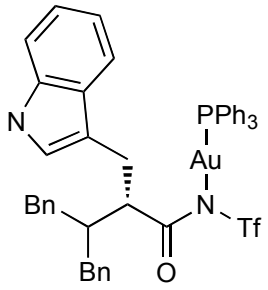
Methyl 2-acetylhept-6-ynoate (50 mg, 0,27 mmol) was placed in dried round bottom flask under nitrogen. The appropriate dry solvent (0.69 ml, 0.4M) was added and the reaction mixture stirred for 2 minutes. The catalyst (16.5 mg, 0.014 mmol, 0.05 mol %) was added and the reaction mixture stirred for the appropriate time at the corresponding temperature. The solvent was concentrated under reduced pressure. Purification by column chromatography ([99:1], cyclohexane : ethyl acetate) afforded the title compound as colorless yellow oil.

5,8a-dimethyl-7,8,8a,9,10,10a-hexahydroanthracen-1-ol (135)



Reagents. (i) catalyst, solvent (see table below).

The starting material was prepared following Michelet procedure. All data is identical to that reported.[46]



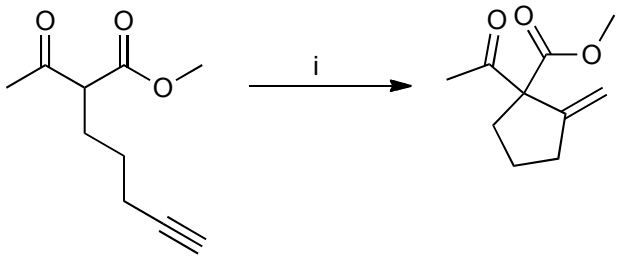
Entry	Mol%	Solvent	Time	T [C°]	Yield [%]	$[\alpha]_D$
1	5	CH_2Cl_2	5 Days	RT	46	0

Procedure

(*E*)-2-(3-methyloct-2-en-6-yn-1-yl)phenol (50 mg, 0,24 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.48 ml, 0.5M) was added and the mixture stirred for 2 minutes. The catalyst (11.6 mg, 0.011mmol, 0.05 %mol) was added and the reaction mixture stirred 5 days at room temperature.

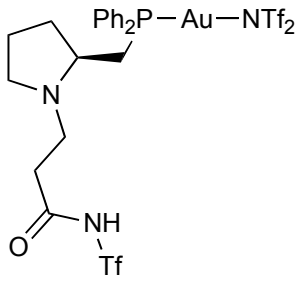
The solvent was concentrated under reduced pressure. Purification by column chromatography ([99:1], cyclohexane : ethyl acetate) afforded the title compound as light yellow oil (23.7 mg, 46%).

Methyl 1-acetyl-2-methylenecyclopentanecarboxylate (17)



Reagents. (i) catalyst, solvent (see table below).

The starting material was prepared following Fournet procedure.[105] All data is identical to that reported.[35]



Entry	Mol%	Solvent	Time	T [C°]	Yield [%]	Starting Material [%]	$[\alpha]_D$
1	1+1[a]	CH_2Cl_2	2 Days	RT	73	16	-3.2
2	2	CH_2Cl_2	2 Days	RT	65	21	-3.0
3	1	$(CH_2)_2Cl_2$	24h	50	58	40	-1.2
4	-----	$(CH_2)_2Cl_2$	24h	50	8	78	------

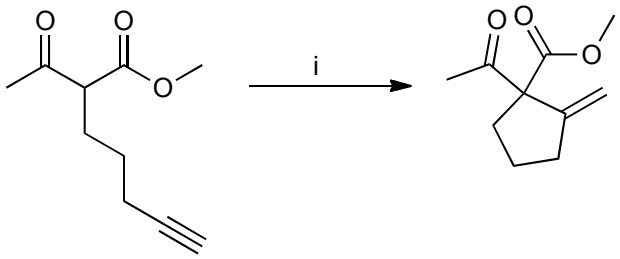
[a] – after 1 day another 1mol% was added

Procedure

Methyl 2-acetylhept-6-ynoate (50 mg, 0,27 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.69 ml, 0.4M) was added and the mixture was stirred for 2 minutes. The catalyst was added and reaction mixture was stirred for the appropriate time at corresponding temperature.

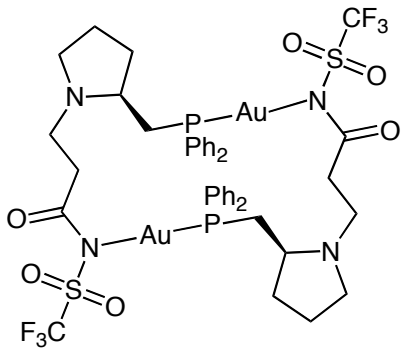
The solvent was concentrated under reduced pressure. Purification by column chromatography ([95:5], PET : ethyl acetate or diethyl ether) afforded the title compound as colorless yellow oil.

Methyl 1-acetyl-2-methylenecyclopentanecarboxylate (17)



Reagents. (i) catalyst, solvent (see table below).

The starting material was prepared following Fournet procedure.[105] All data is identical to that reported.[35]



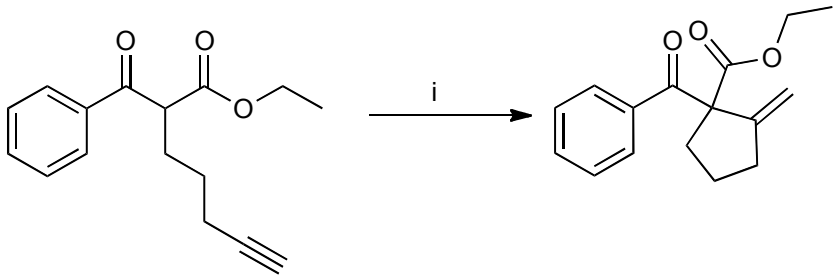
Entry	Mol%	Solvent	Time	T [C°]	Yield [%]	Starting Material [%]	$[\alpha]_D$
1	5	CH_2Cl_2	5 Days	RT	33	48	2.4
2	5	$(CH_2)_2Cl_2$	14h	70	75	0	3.2
3	----	$(CH_2)_2Cl_2$	14h	70	13	78	0

Procedure

Methyl 2-acetylhept-6-ynoate (50 mg, 0,27 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.69 ml, 0.4M) was added and the mixture was stirred for 2 minutes. The catalyst was added and the reaction mixture stirred for the appropriate time at the corresponding temperature.

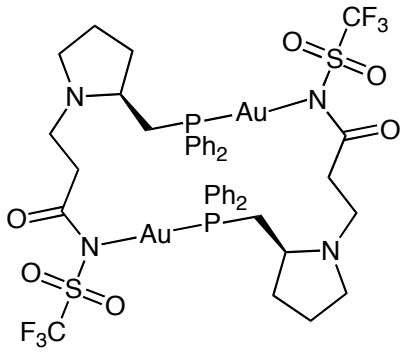
The solvent was concentrated under reduced pressure. Purification by column chromatography ([95:5], PET : ethyl acetate or diethyl ether) afforded the title compound as colorless yellow oil.

Ethyl 1-benzoyl-2-methylenecyclopentanecarboxylate (212)



Reagents. (i) catalyst, solvent (see table below).

The starting material was prepared following Fournet procedure.[105] All data is identical to that reported.[35]



Entry	Mol%	Solvent	Time	T [C°]	Yield [%]	Starting Material [%]	$[\alpha]_D$
1	5	$(CH_2)_2Cl_2$	5 days	70	91	0	8.4

Procedure

Ethyl 2-benzoylhept-6-ynoate (71 mg, 0,27 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.69 ml, 0.4M) was added and the mixture stirred for 2 minutes. The catalyst was added and the reaction mixture stirred for the appropriate time at corresponding temperature.

The solvent was concentrated under reduced pressure. Purification by column chromatography ([95:5], PET : ethyl acetate or diethyl ether) afforded the title compound as colorless oil (65 mg, 91%).

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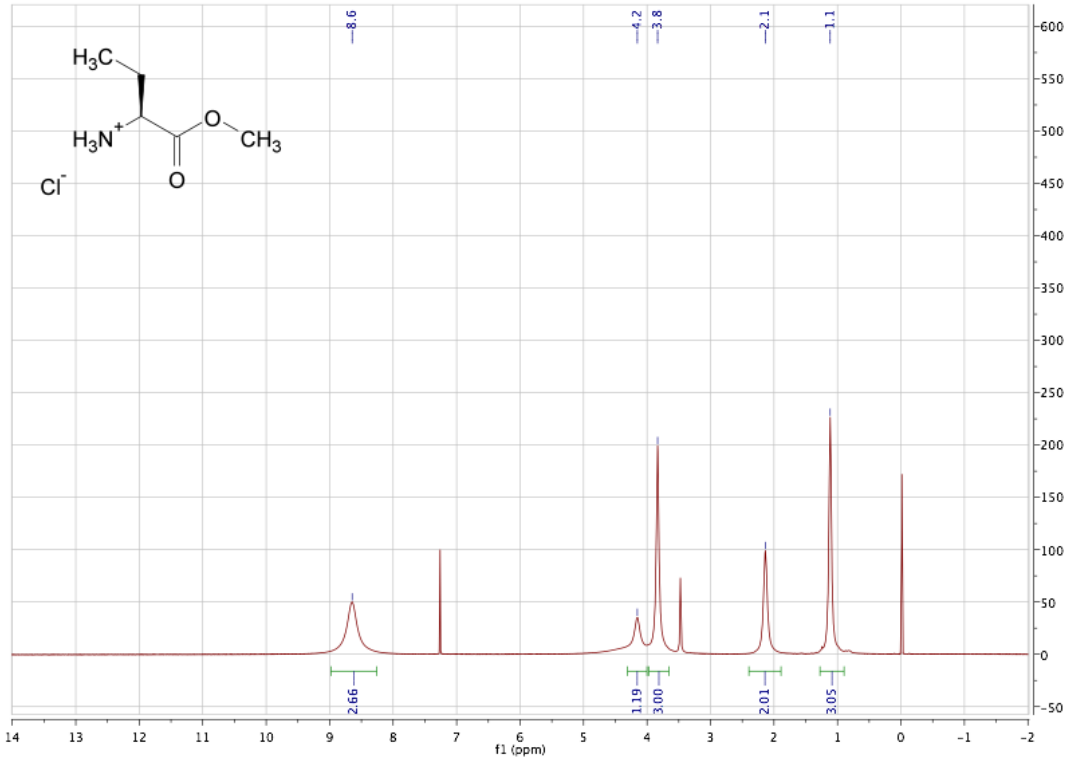
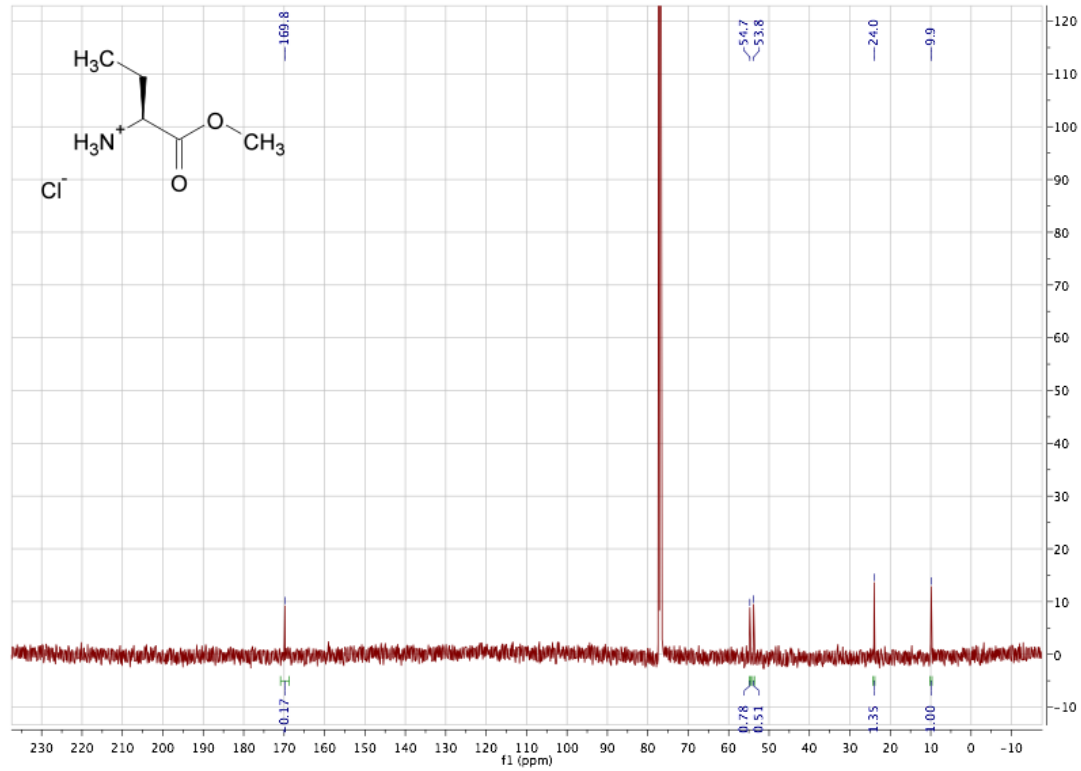
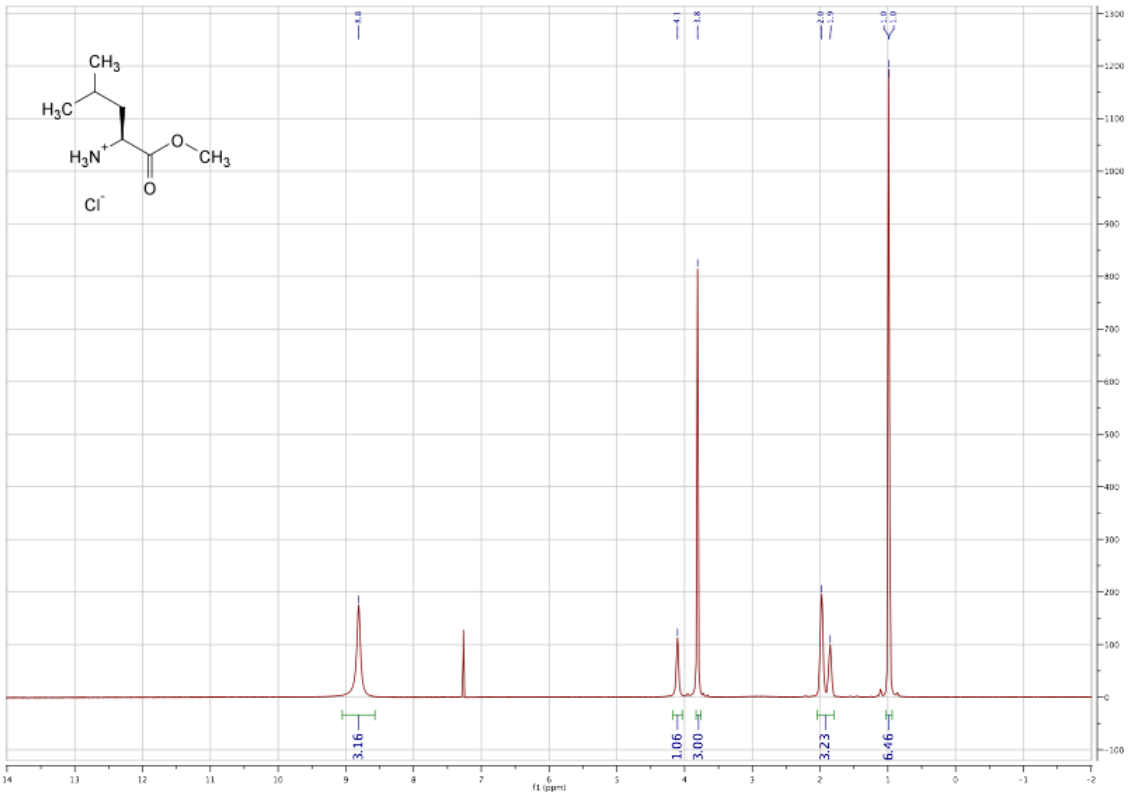
6. NMR Spectra

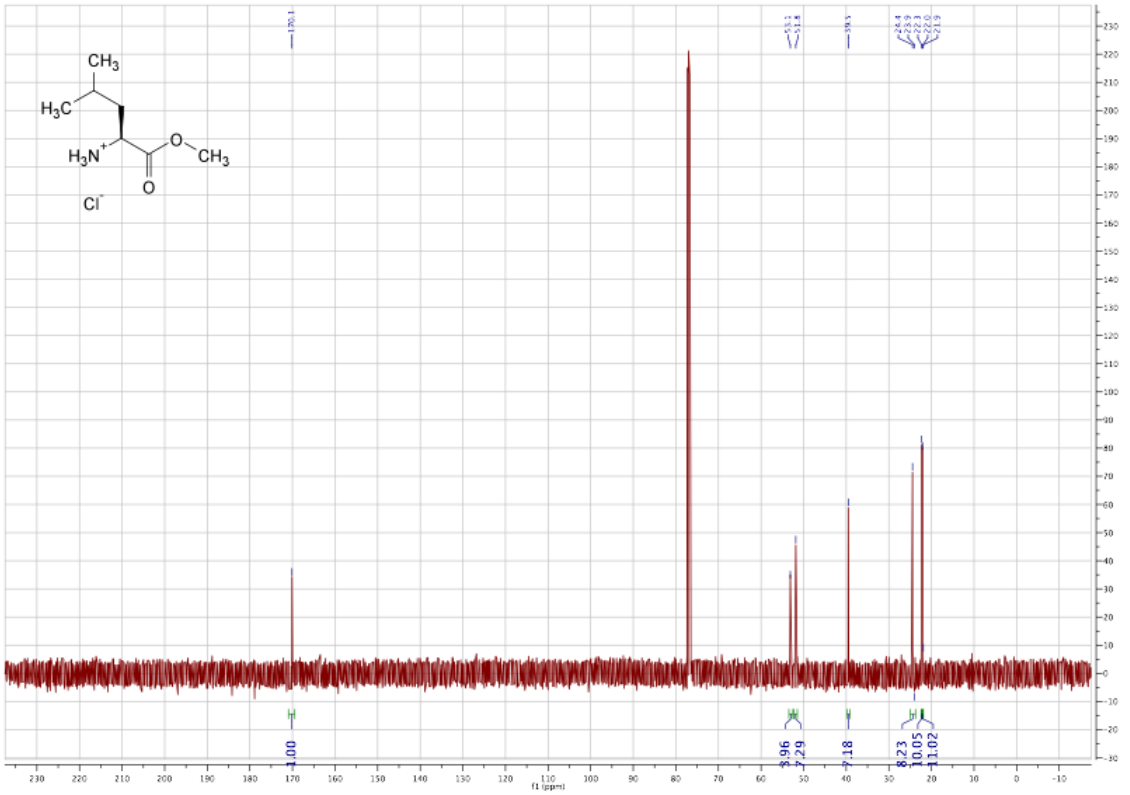
(2*S*)-1-methoxy-1-oxobutan-2-aminium chloride (132a)





(2*S*)-1-methoxy-4-methyl-1-oxopentan-2-aminium chloride (132b)





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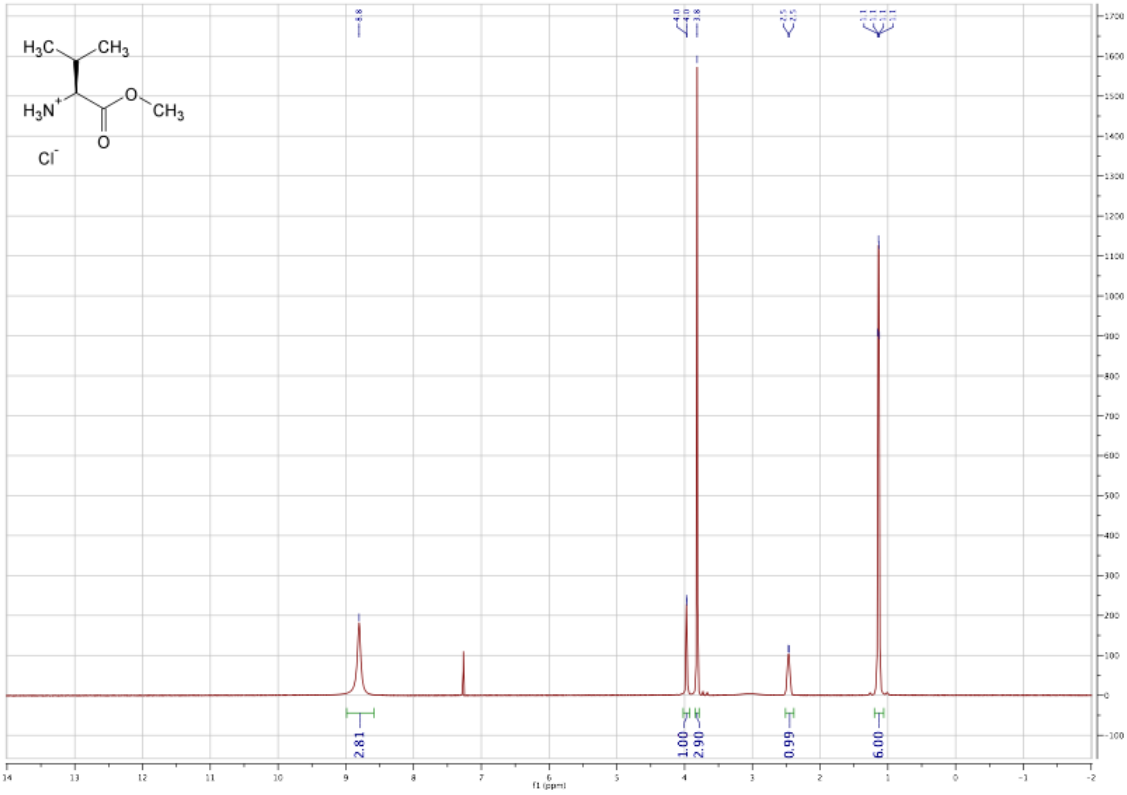
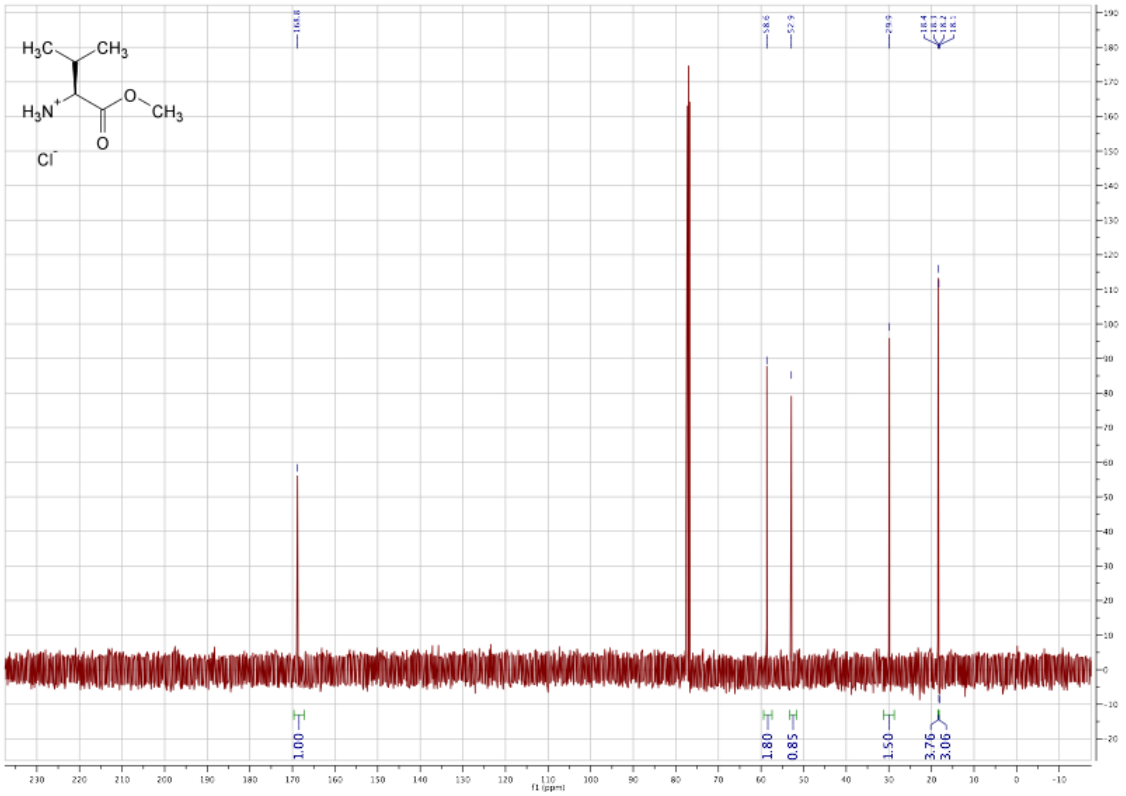
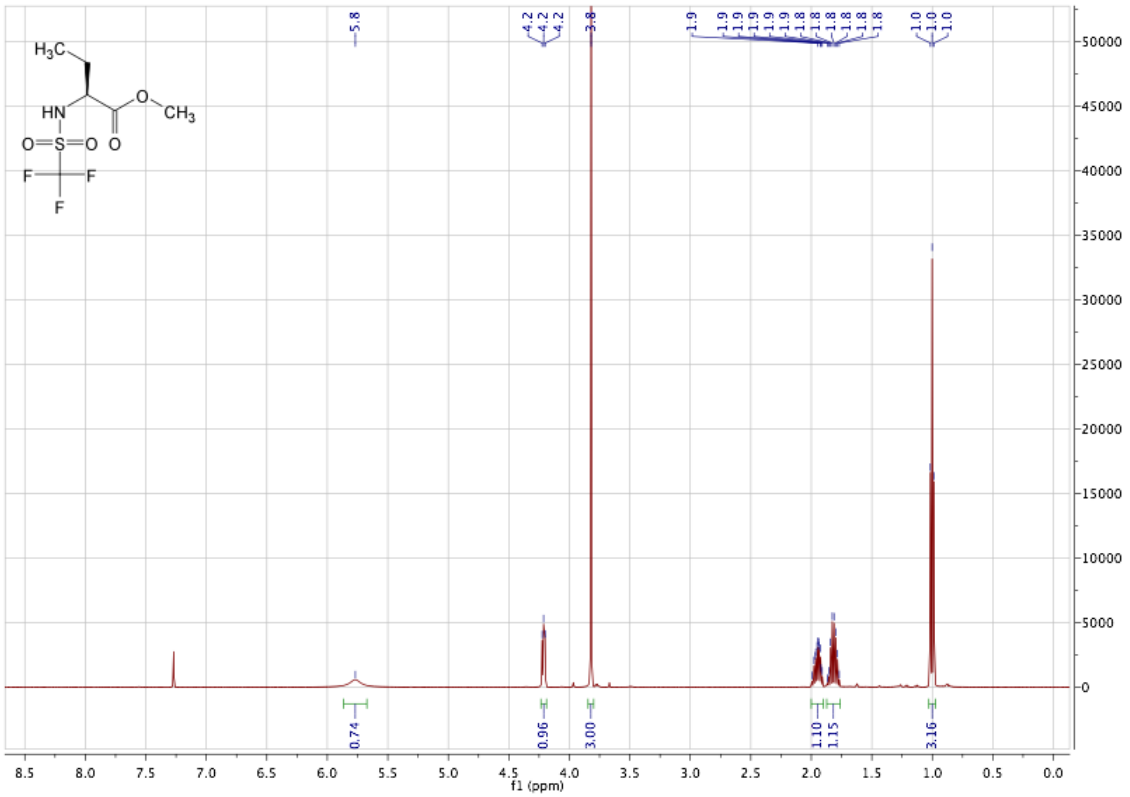
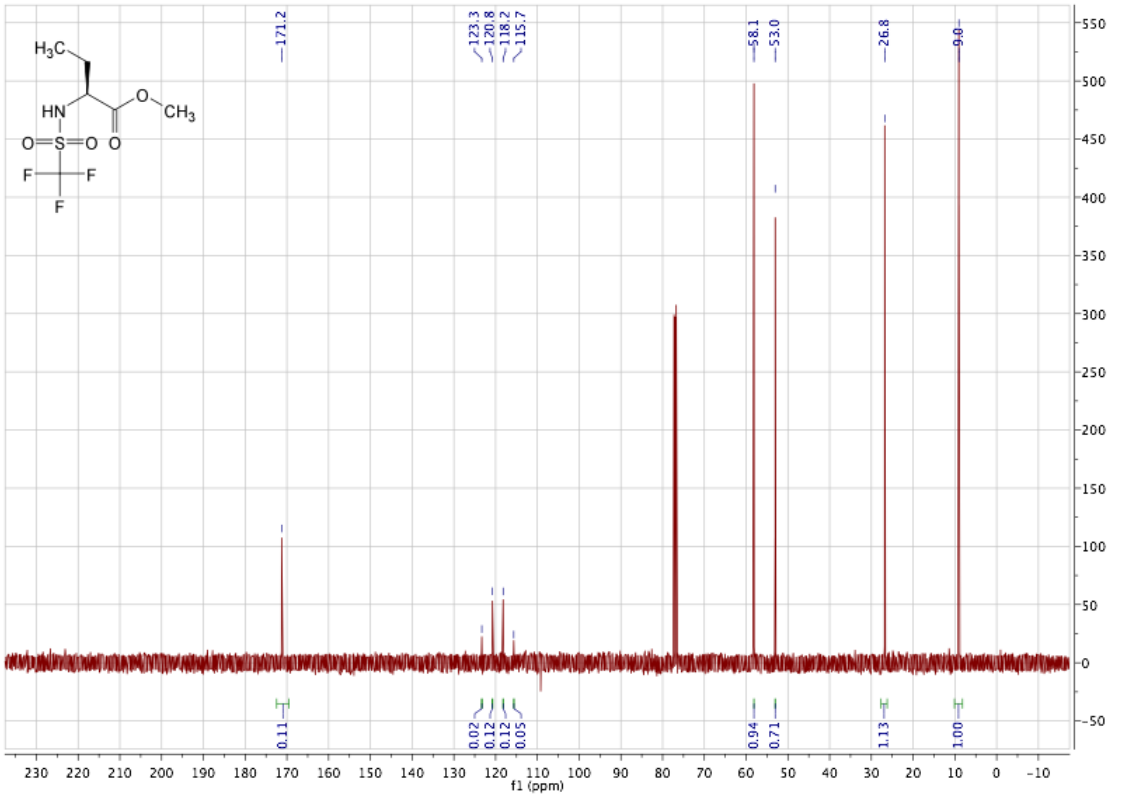


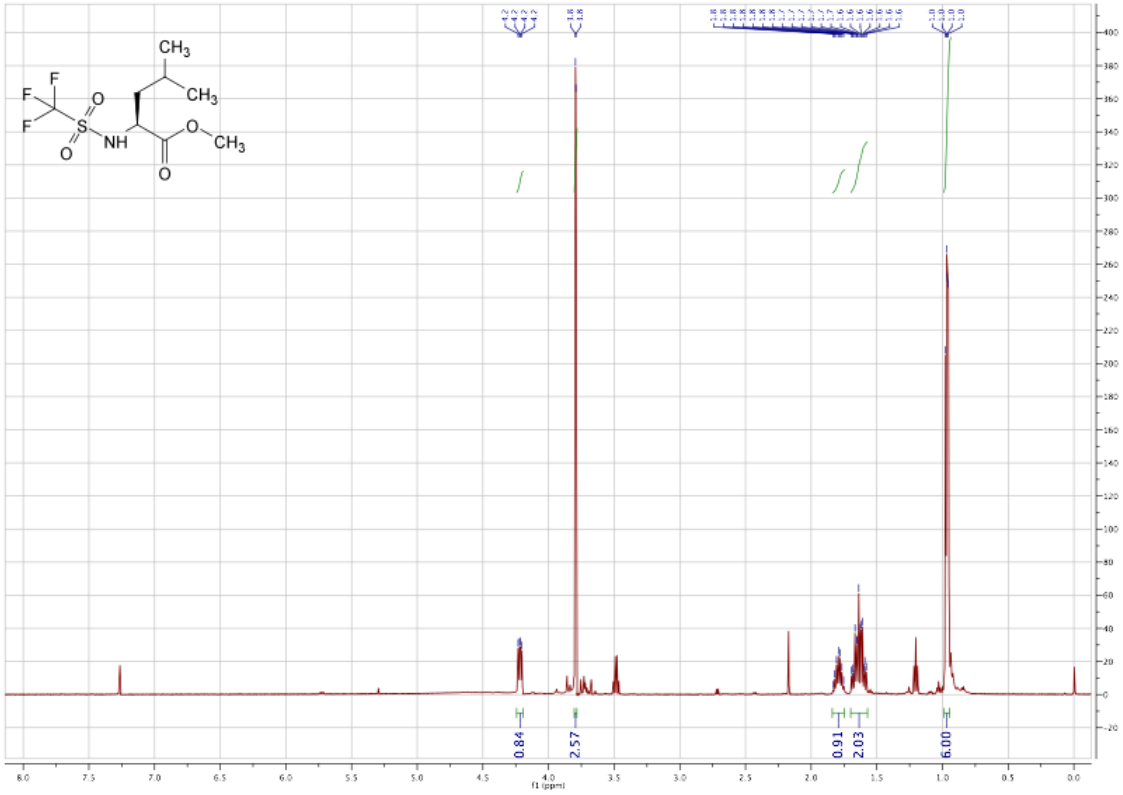


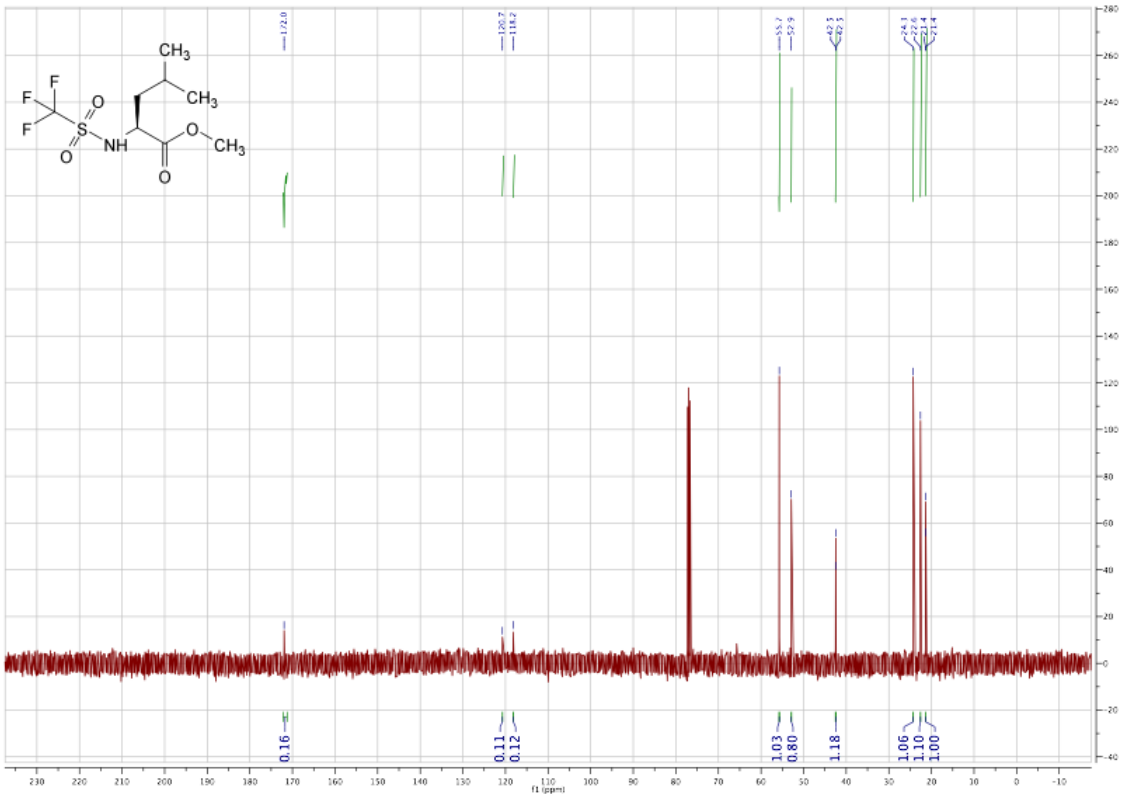
(*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate (133a)





Methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate (133b)





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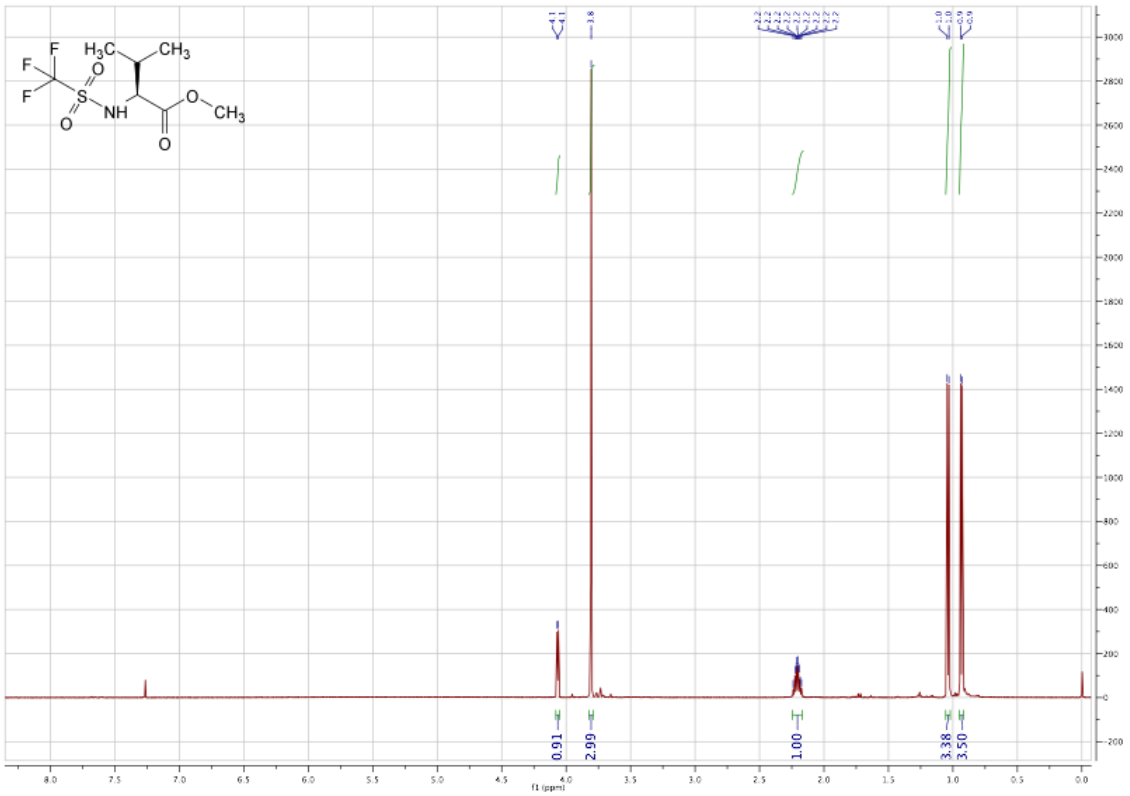
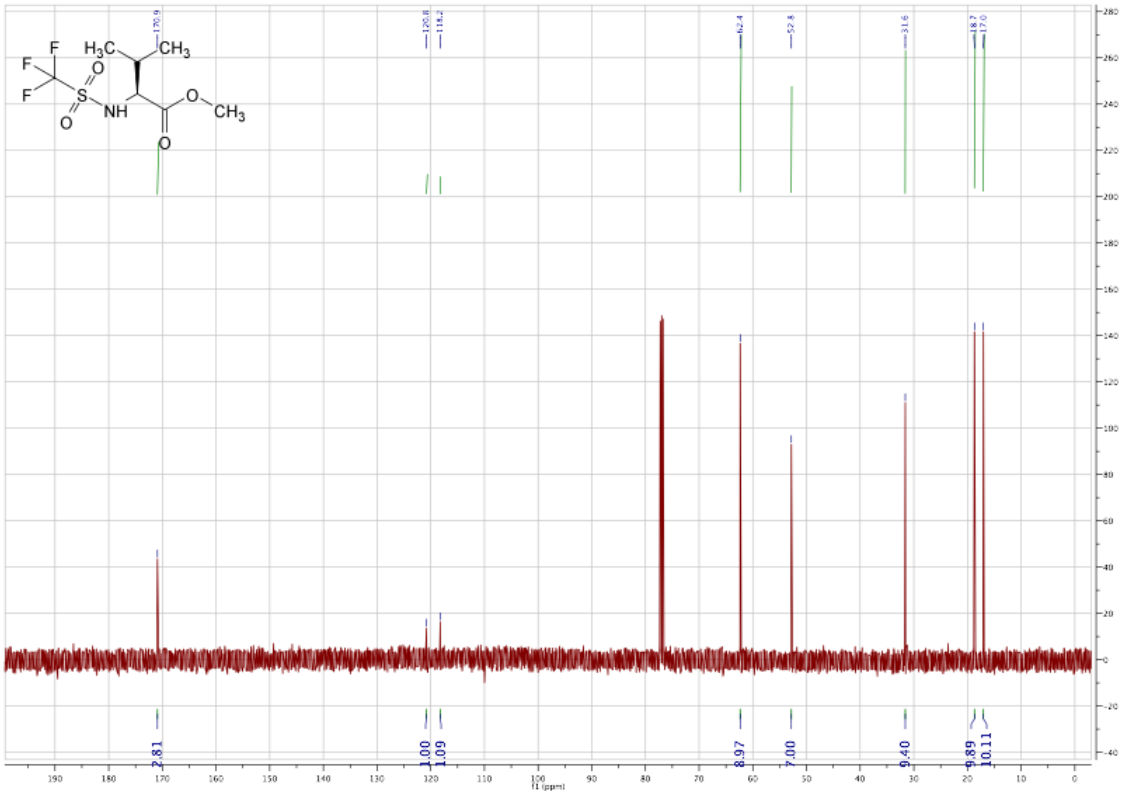
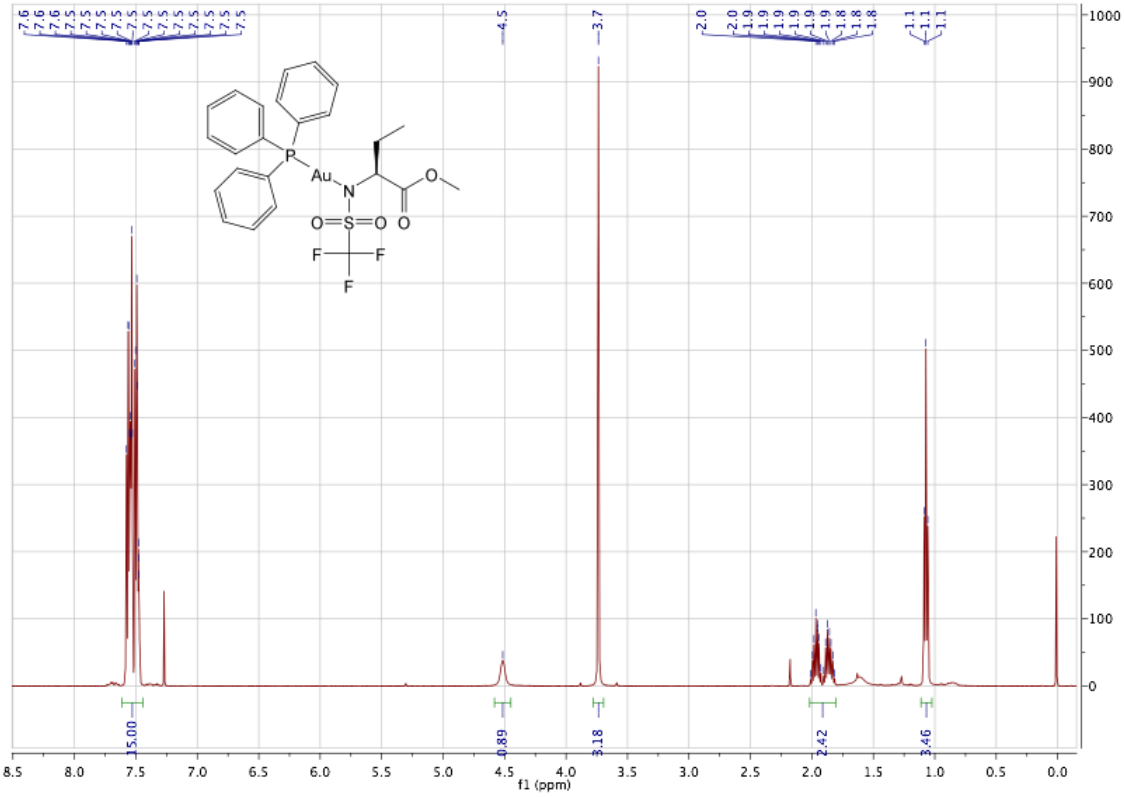
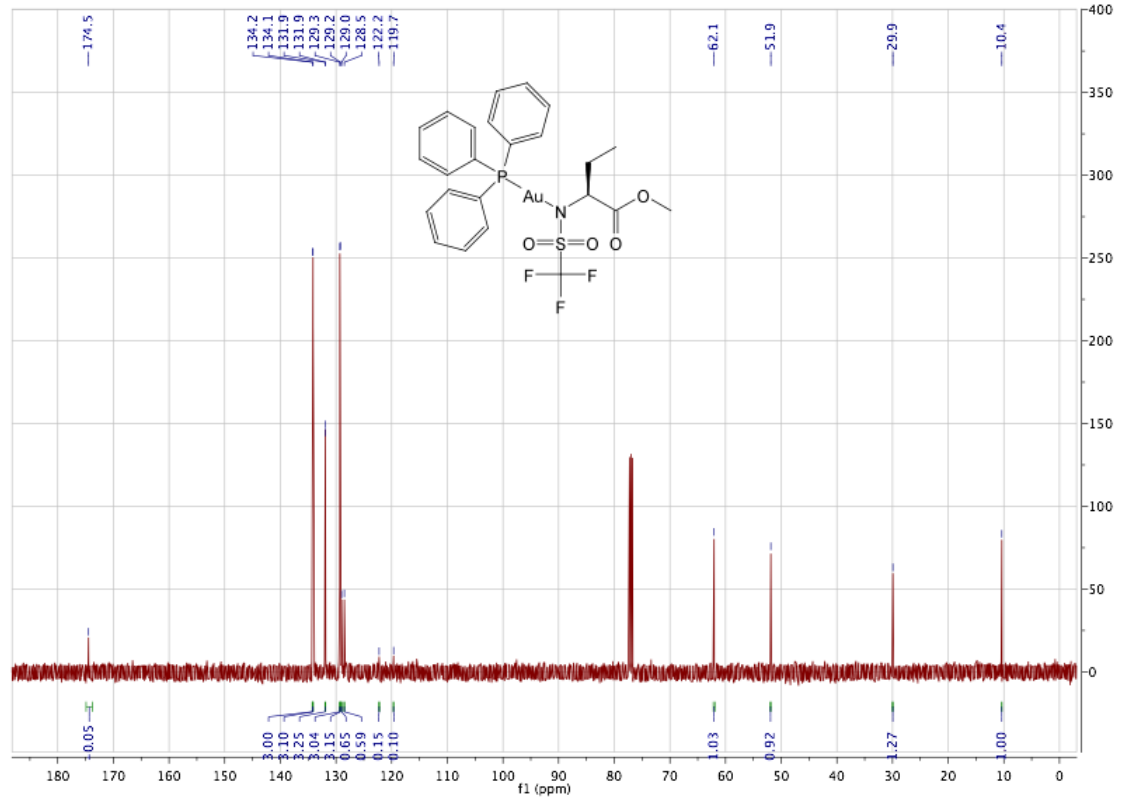


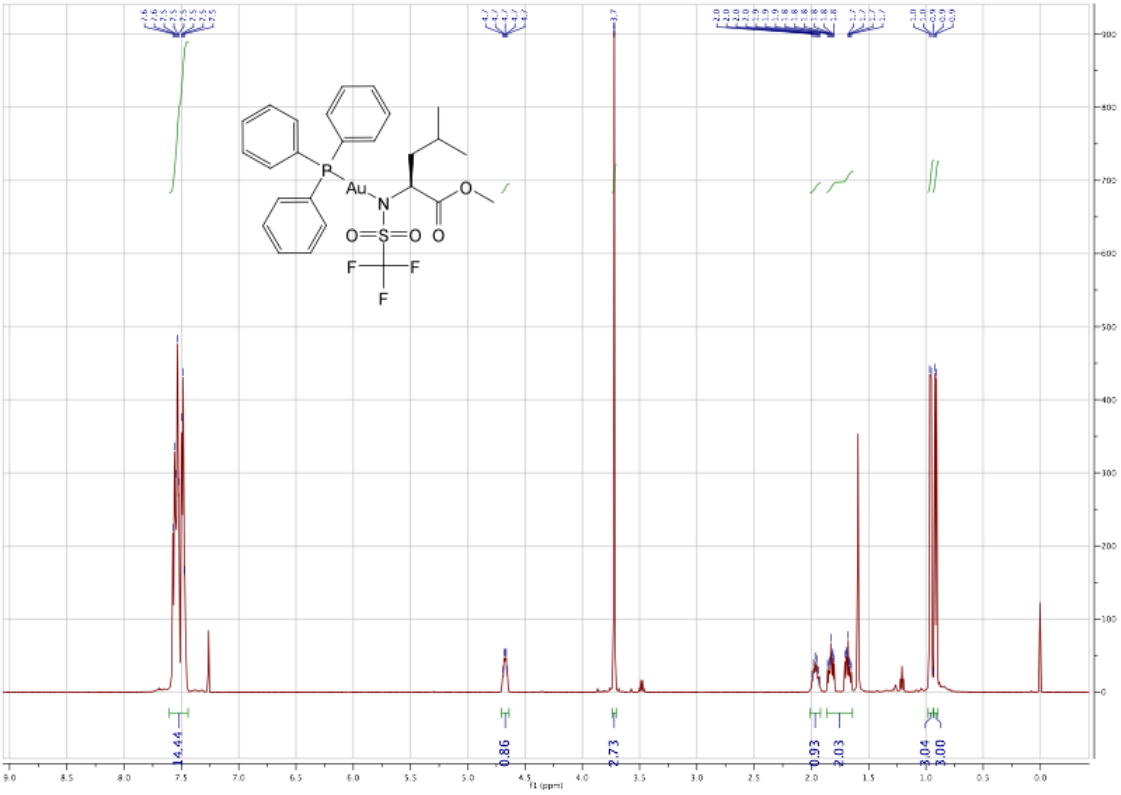


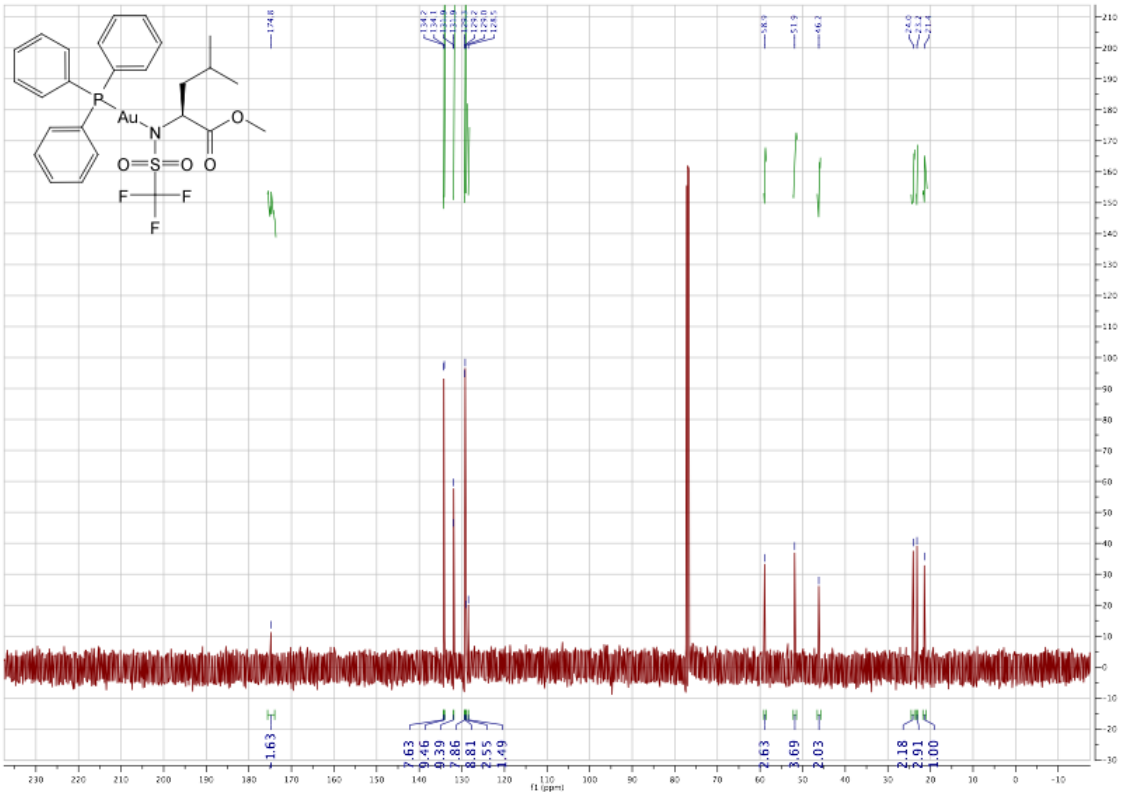
Triphenylphosphine gold (*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate (130a)



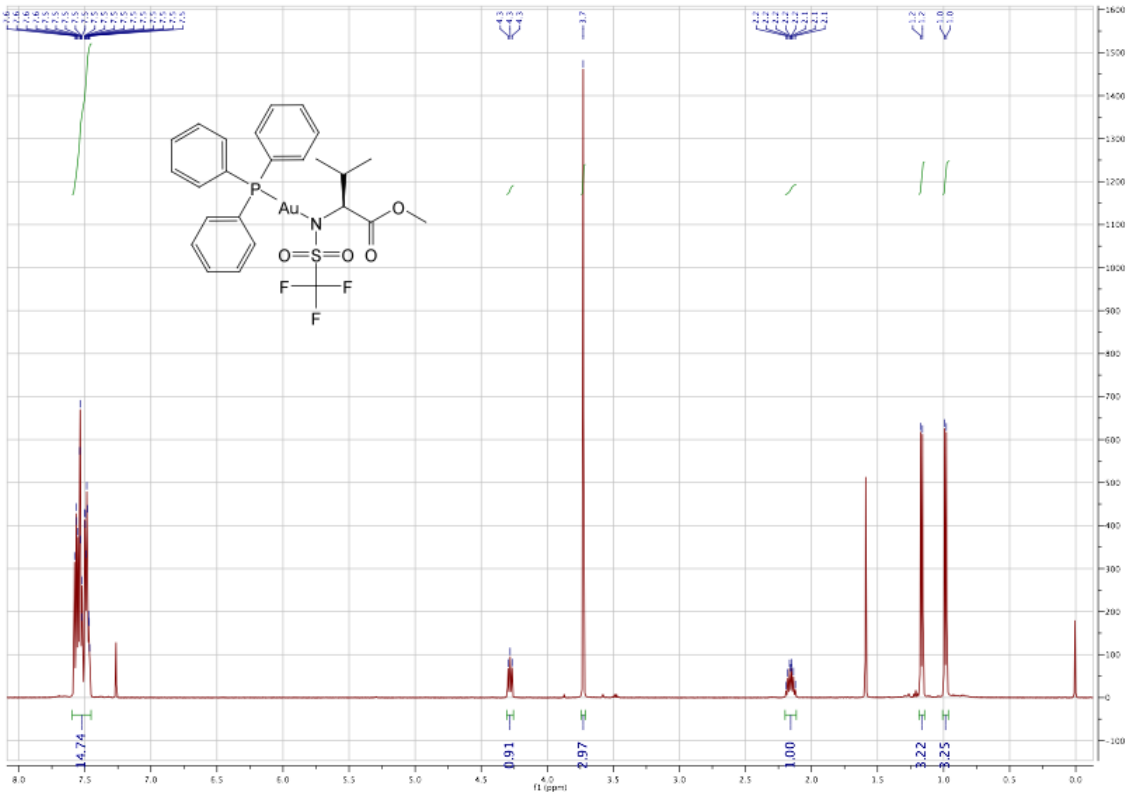


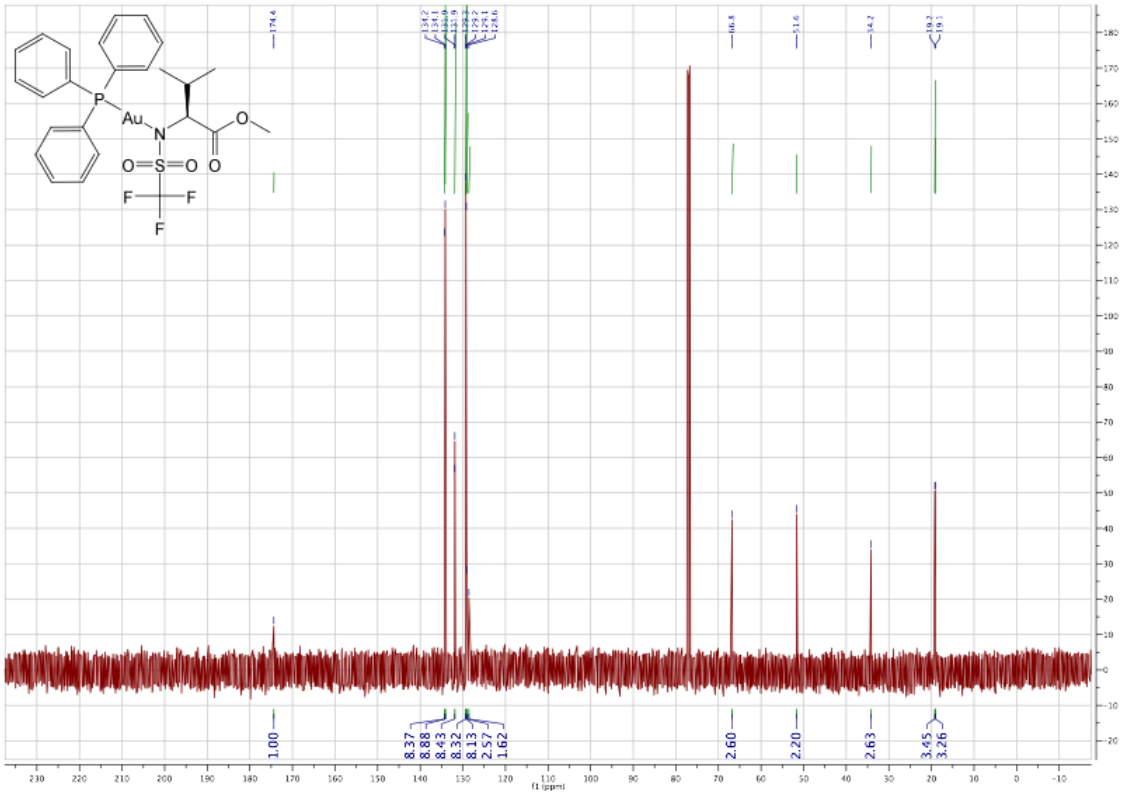
Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate (130b)



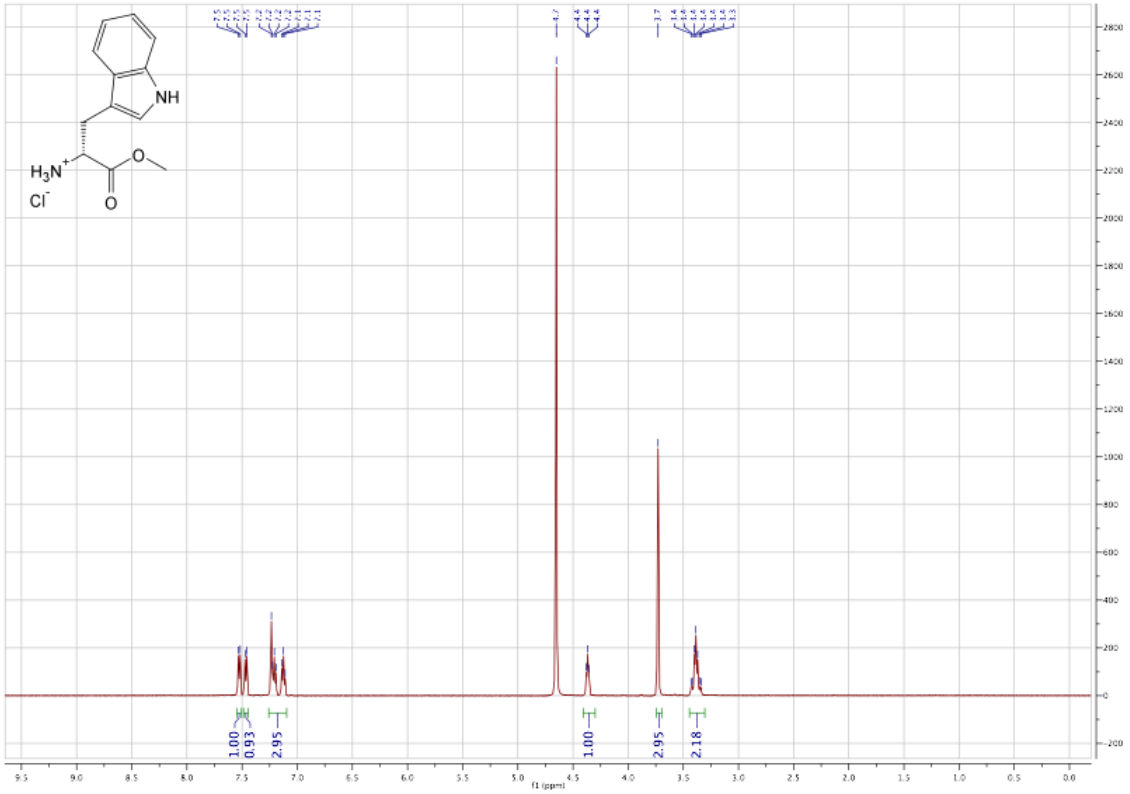


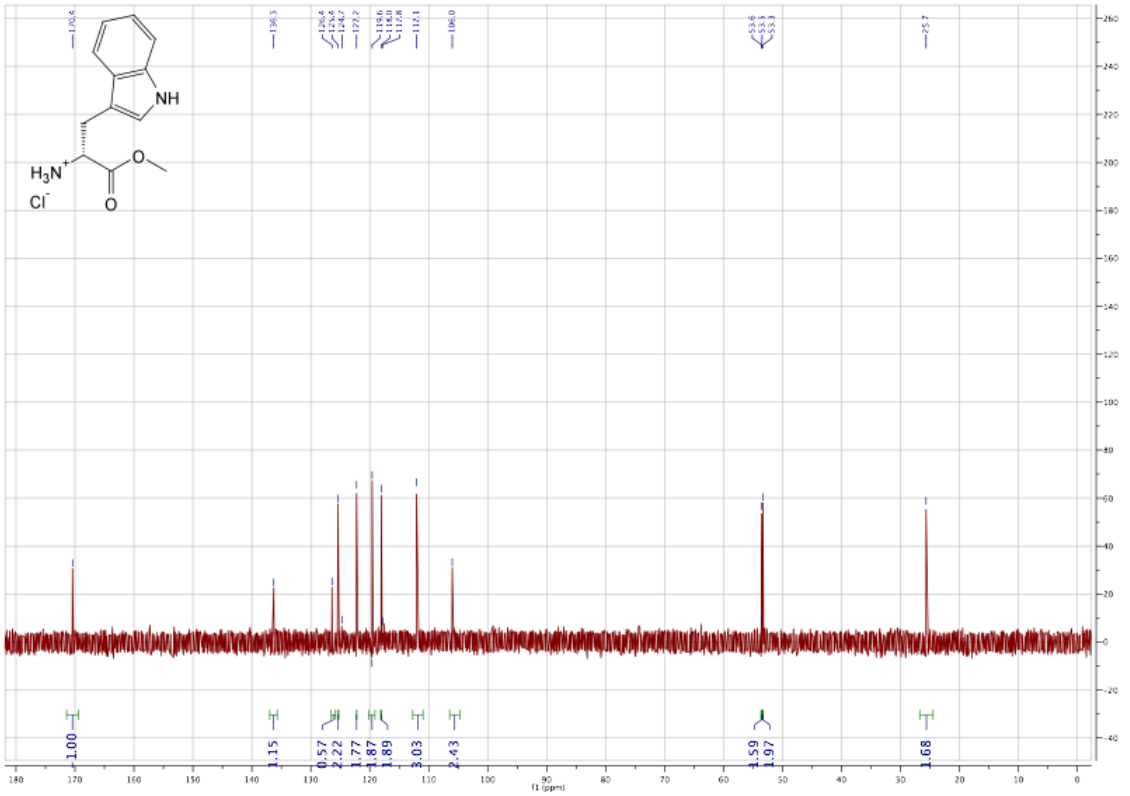
Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-valinate (130c)





(2*R*)-3-(1*H*-indol-3-yl)-1-methoxy-1-oxopropan-2-aminium chloride (132d)





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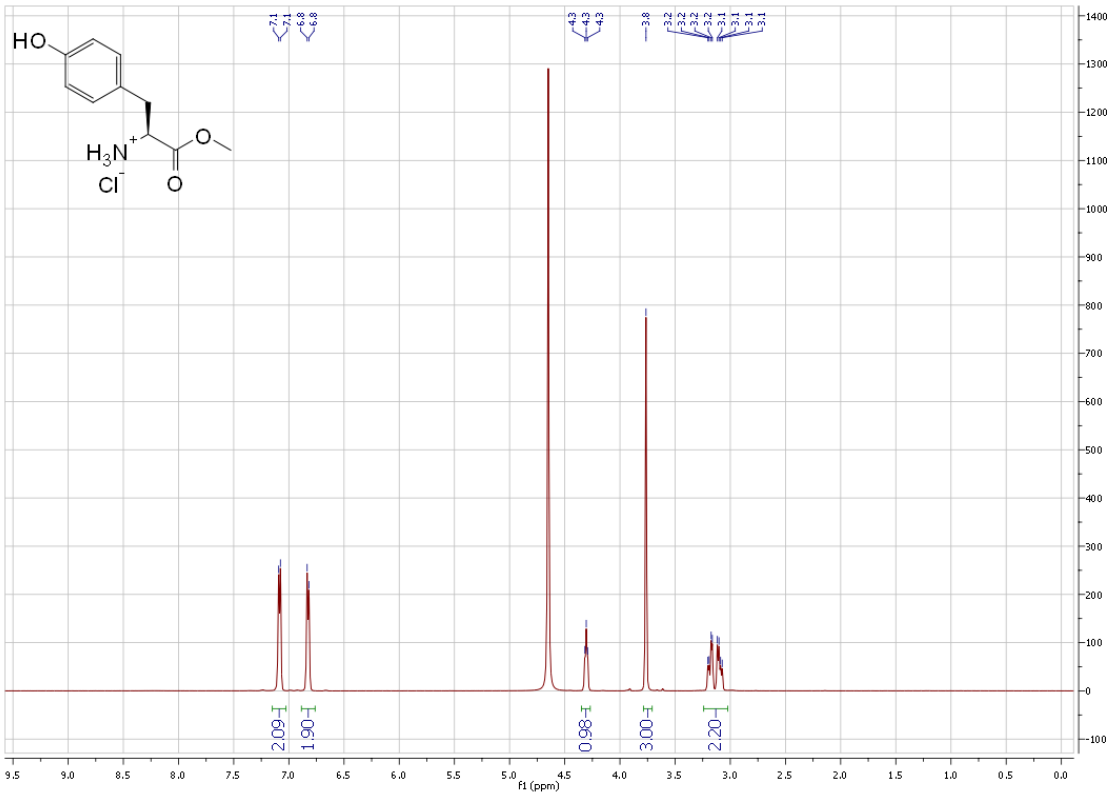
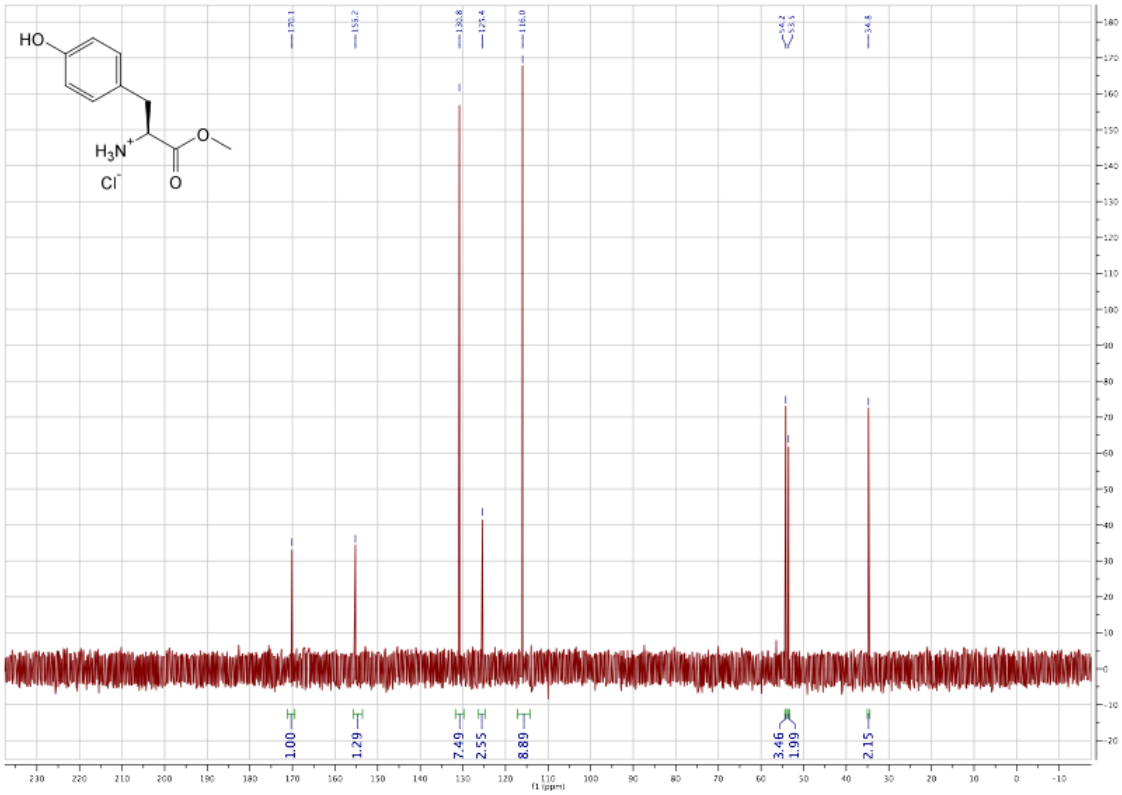
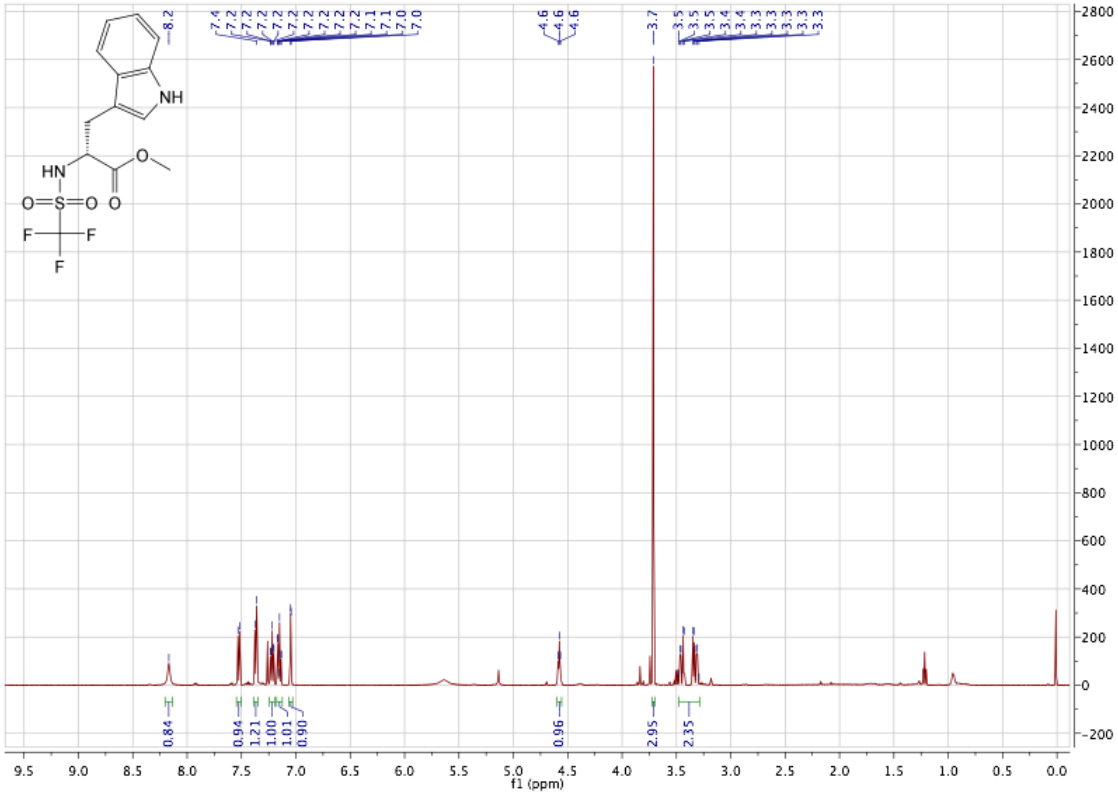
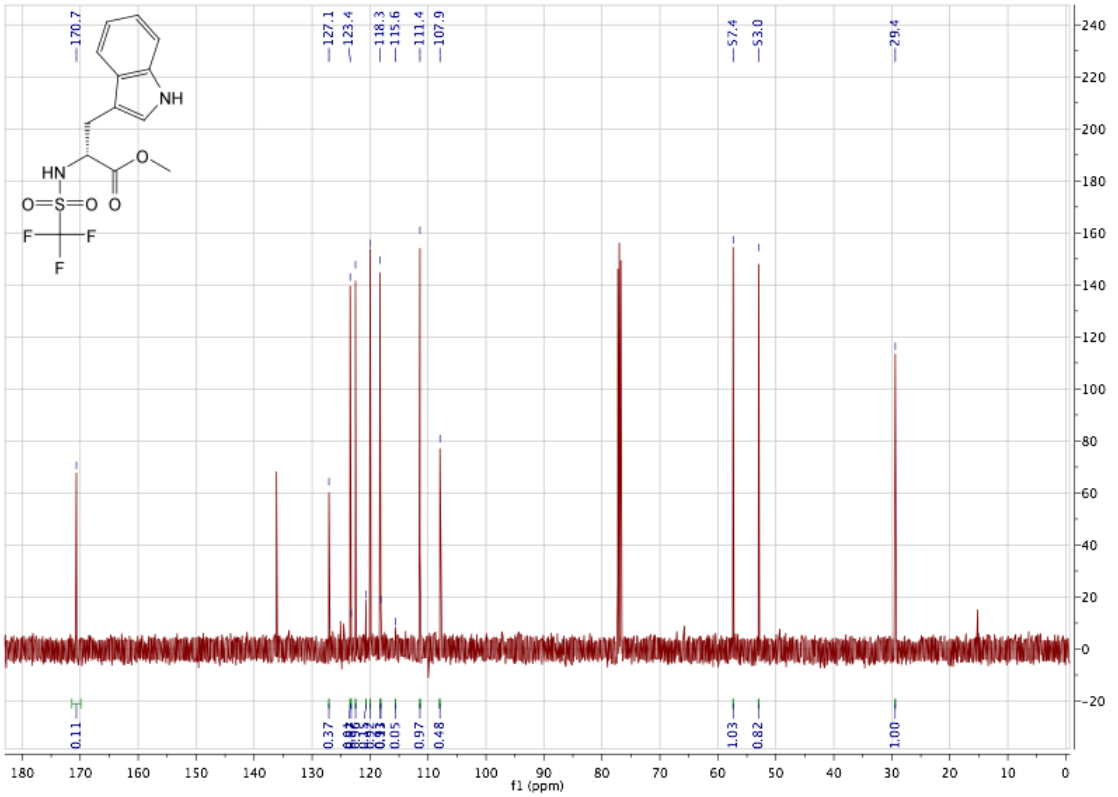




Methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate (133d)





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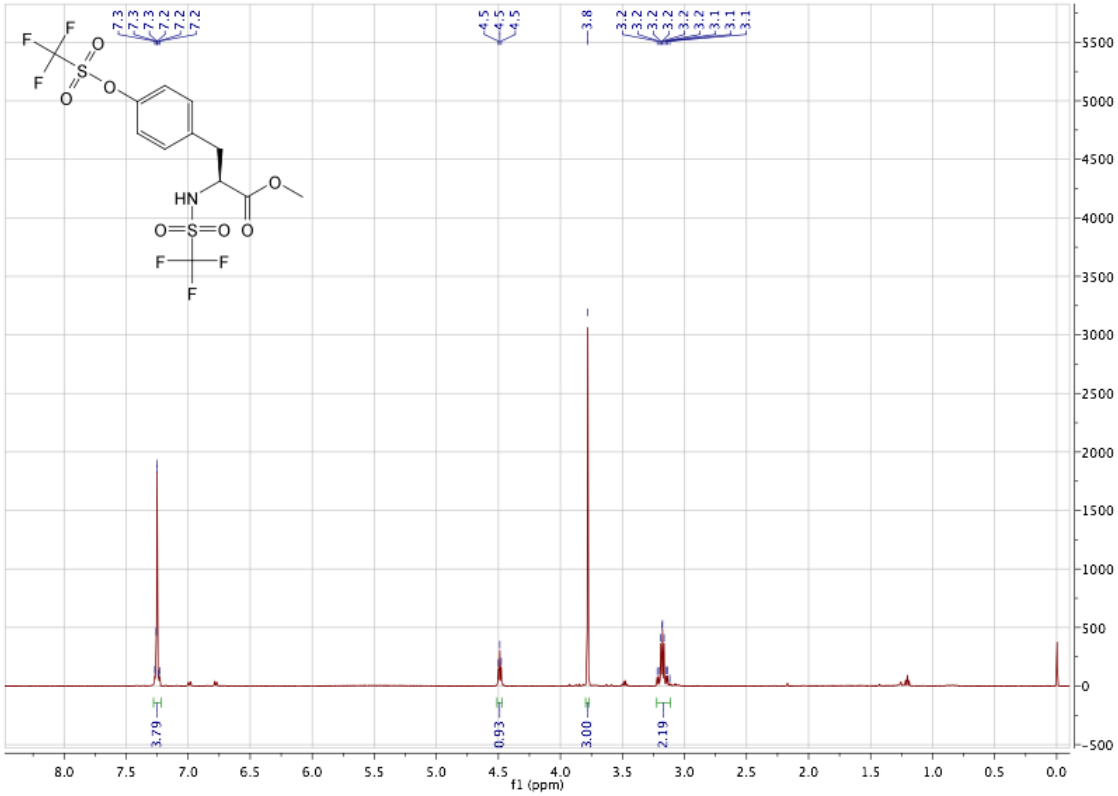
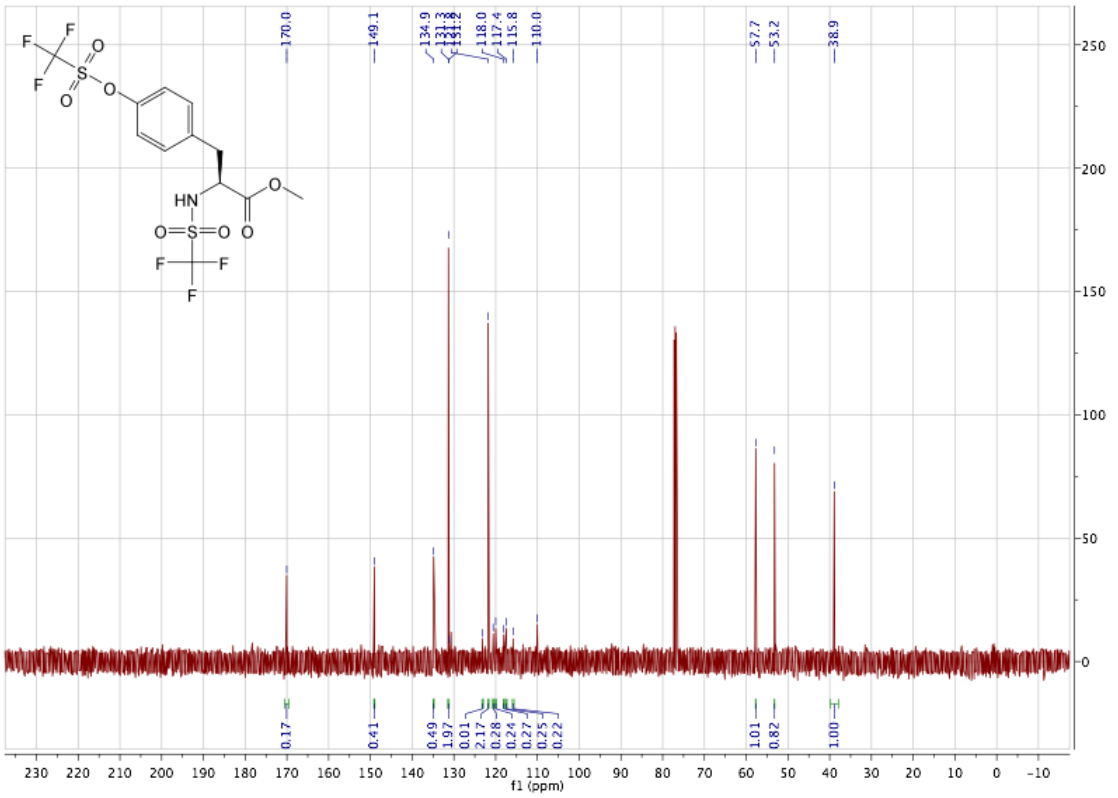
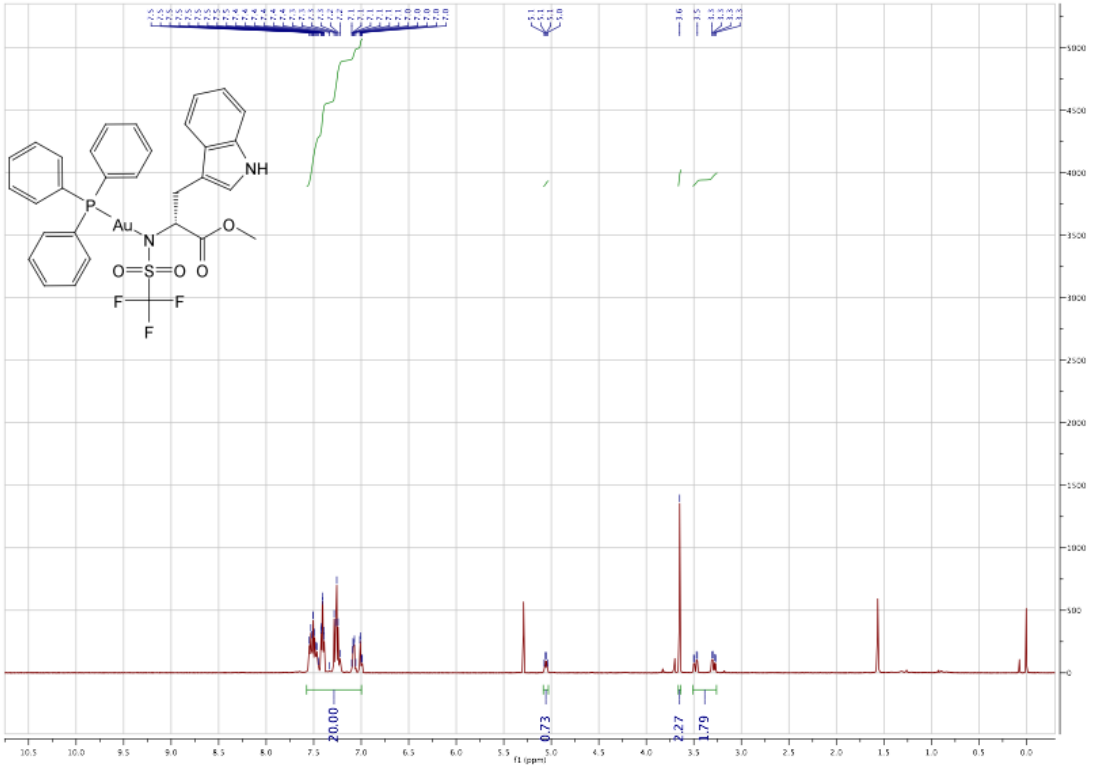
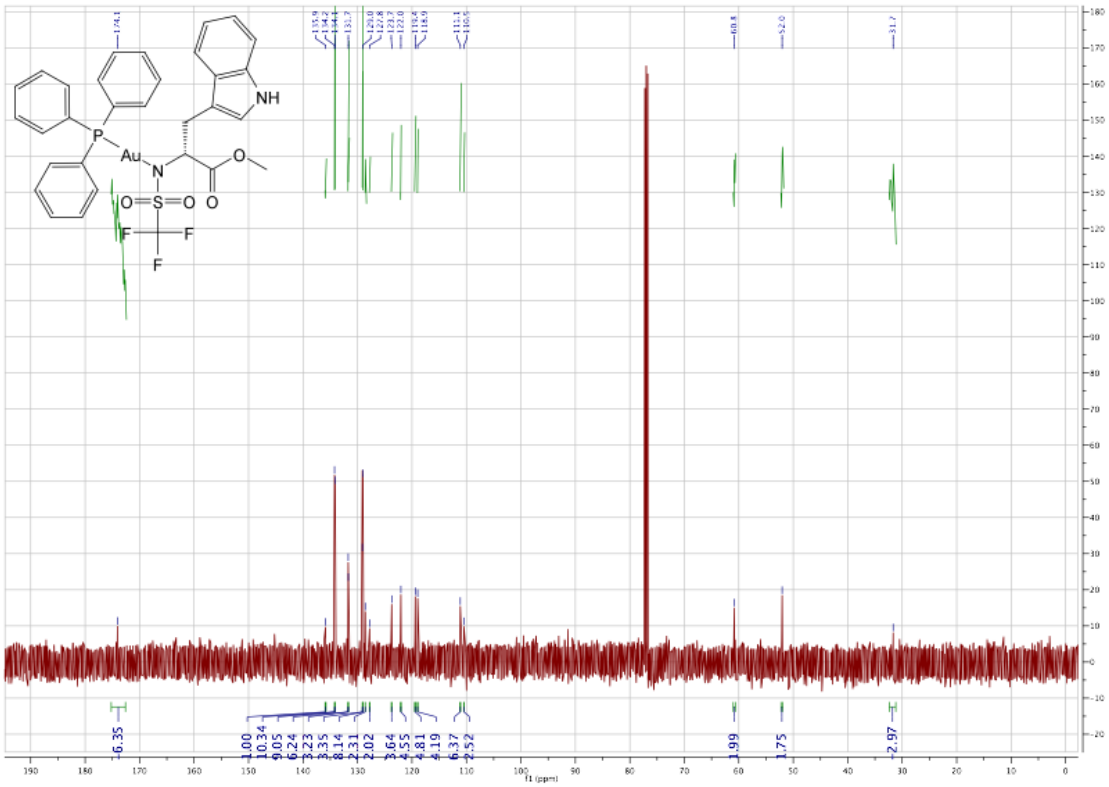


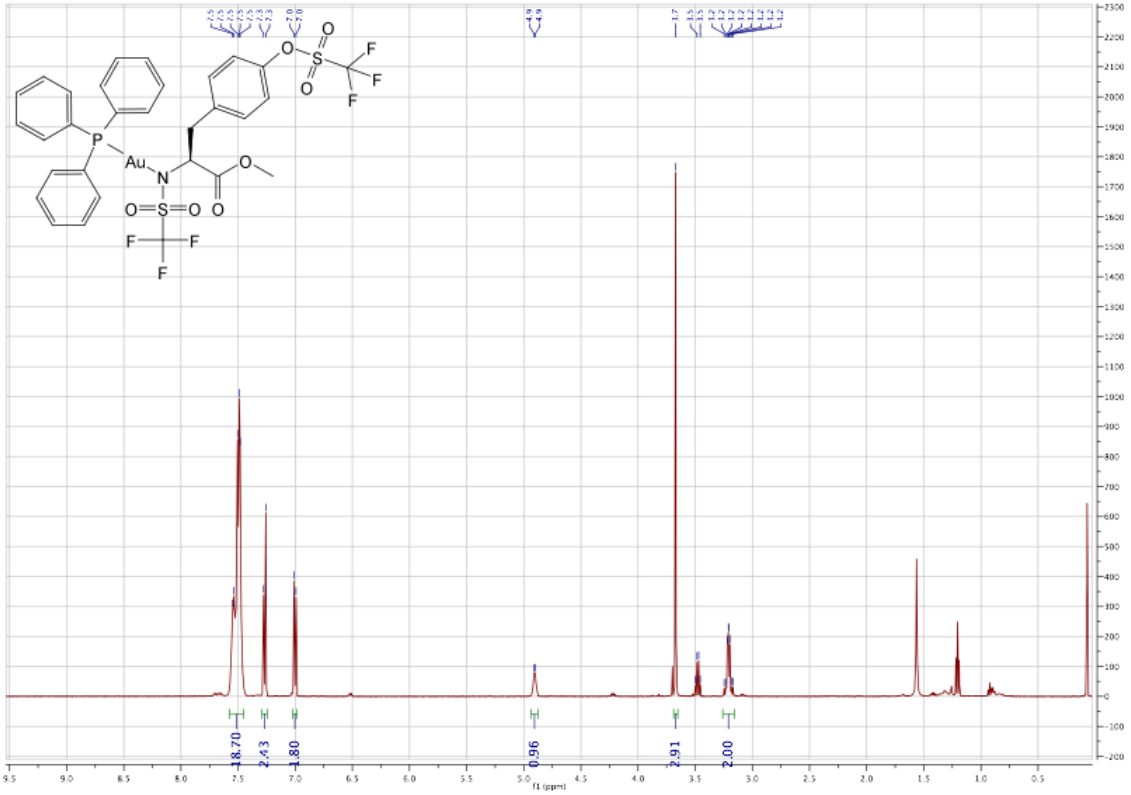


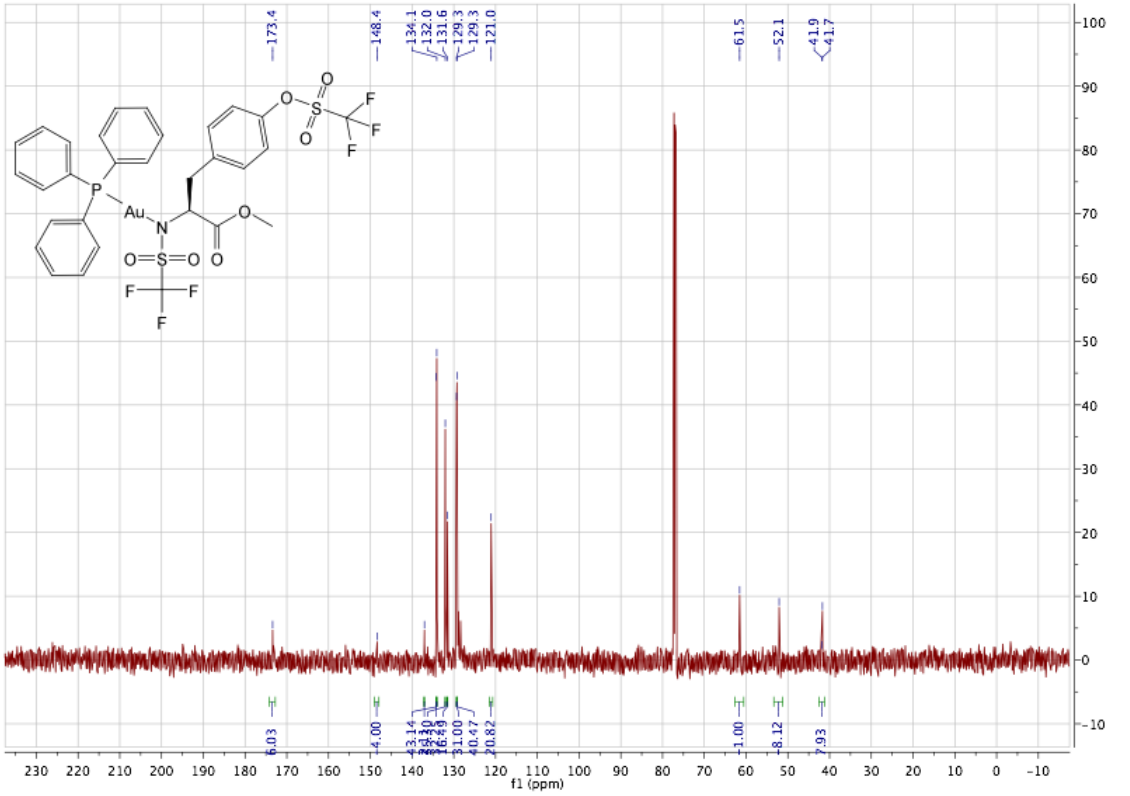
Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate (130d)



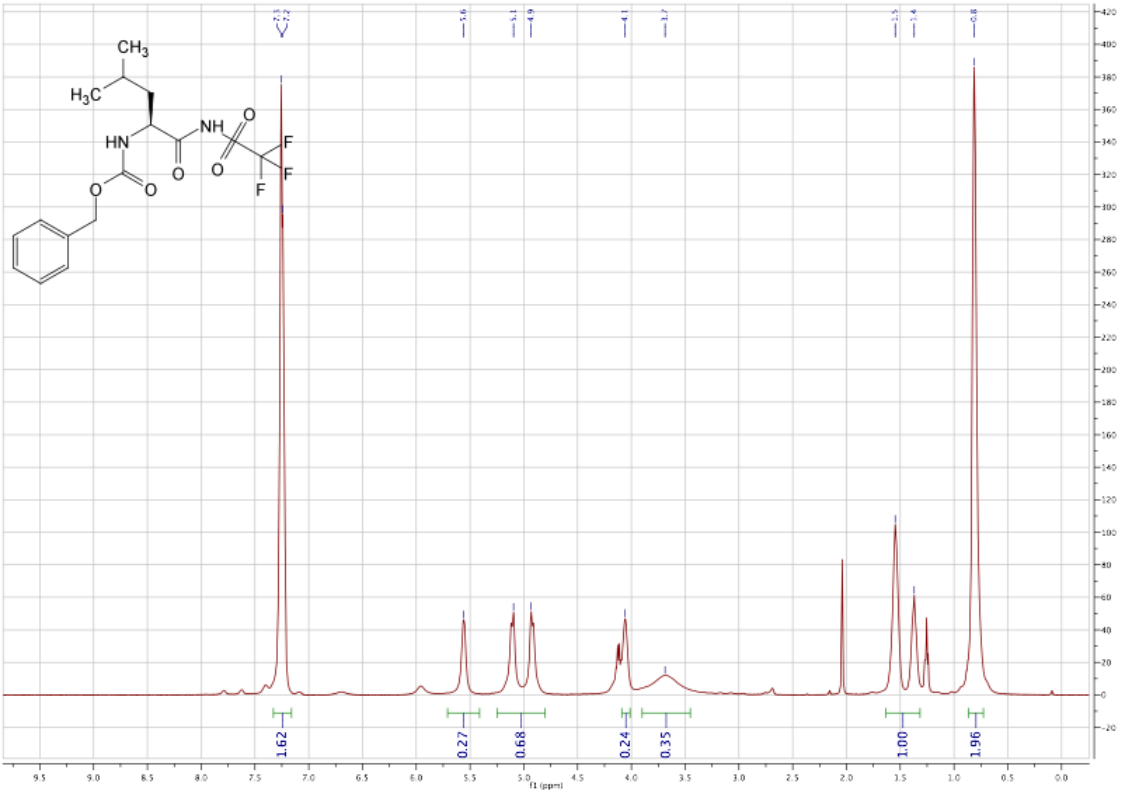


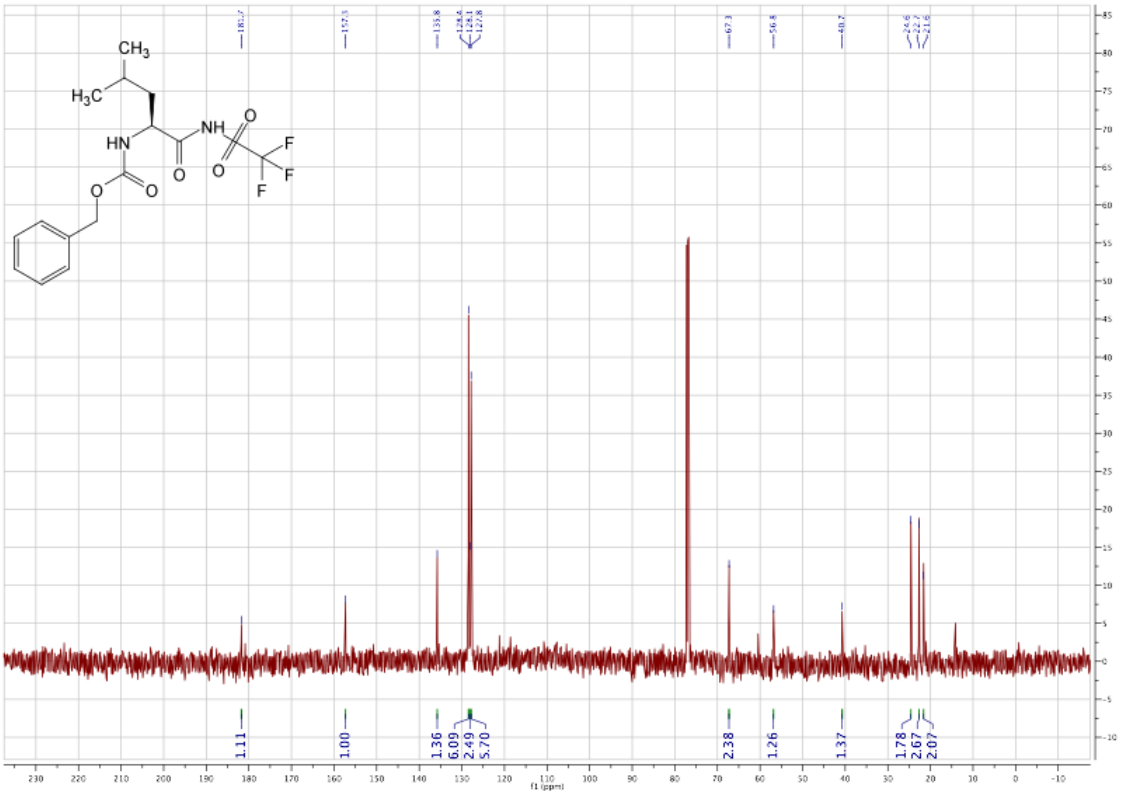
Triphenylphosphine gold (*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido)propanoate (130e)



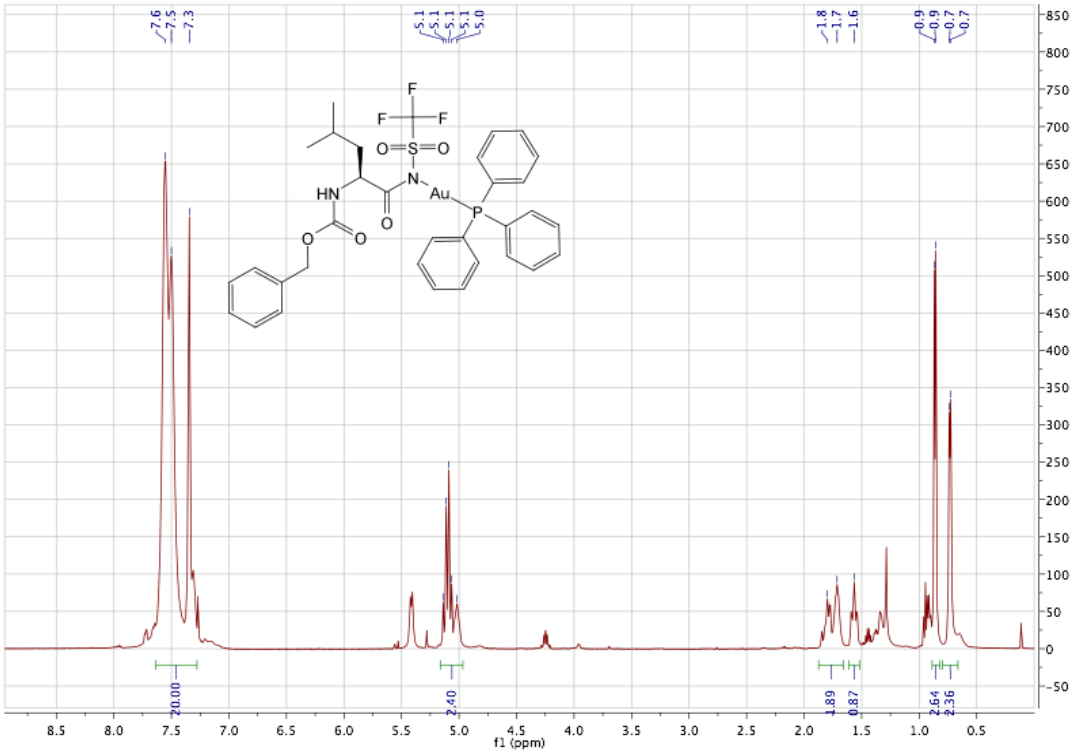


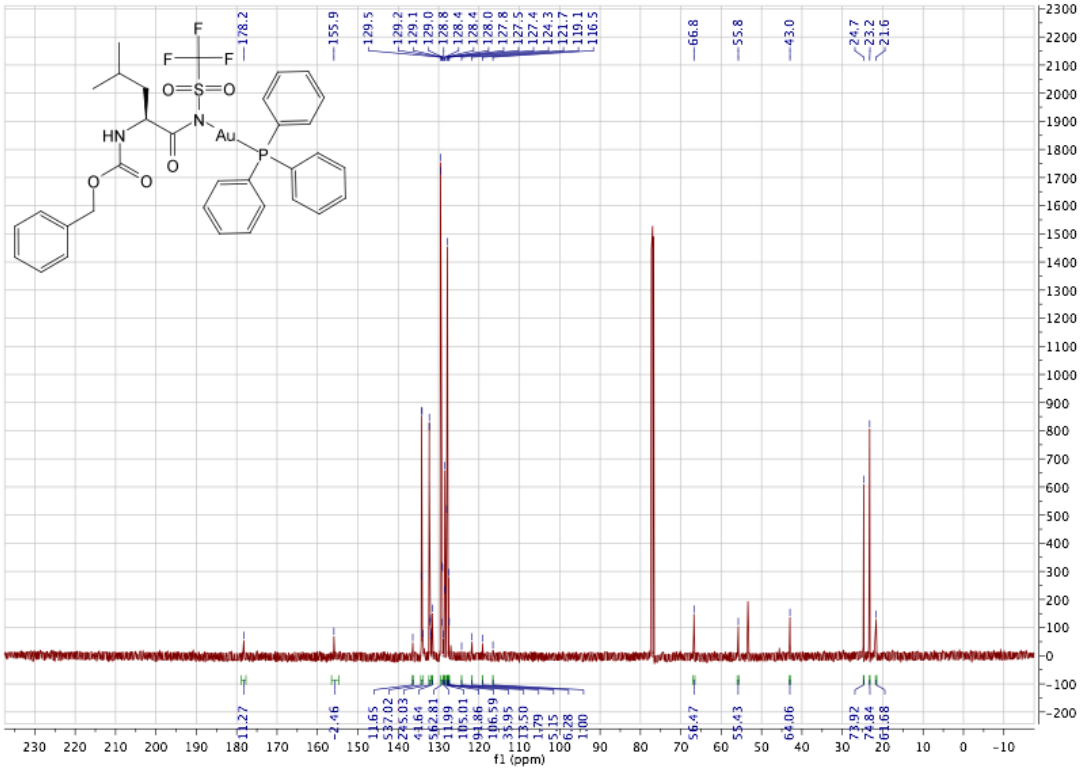
N^2-[(benzyloxy)carbonyl}-N^1-[(trifluoromethyl)sulfonyl]-(*L*)-leucinamide (147)



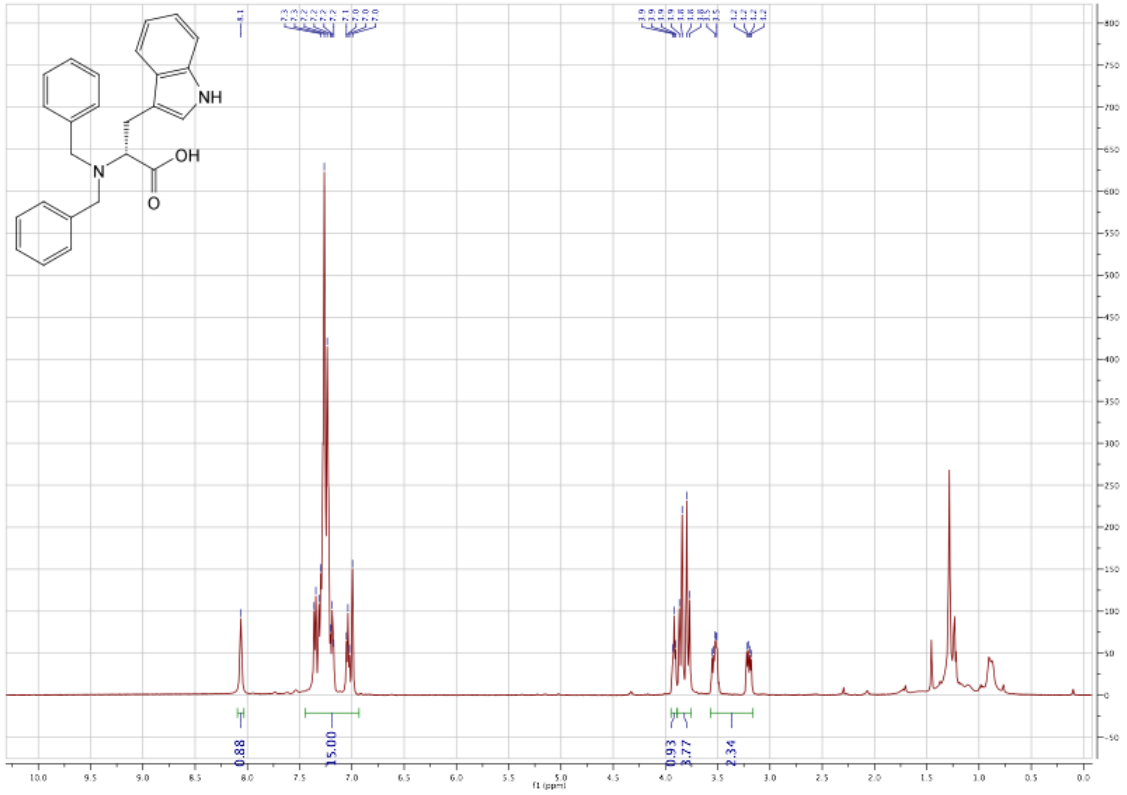


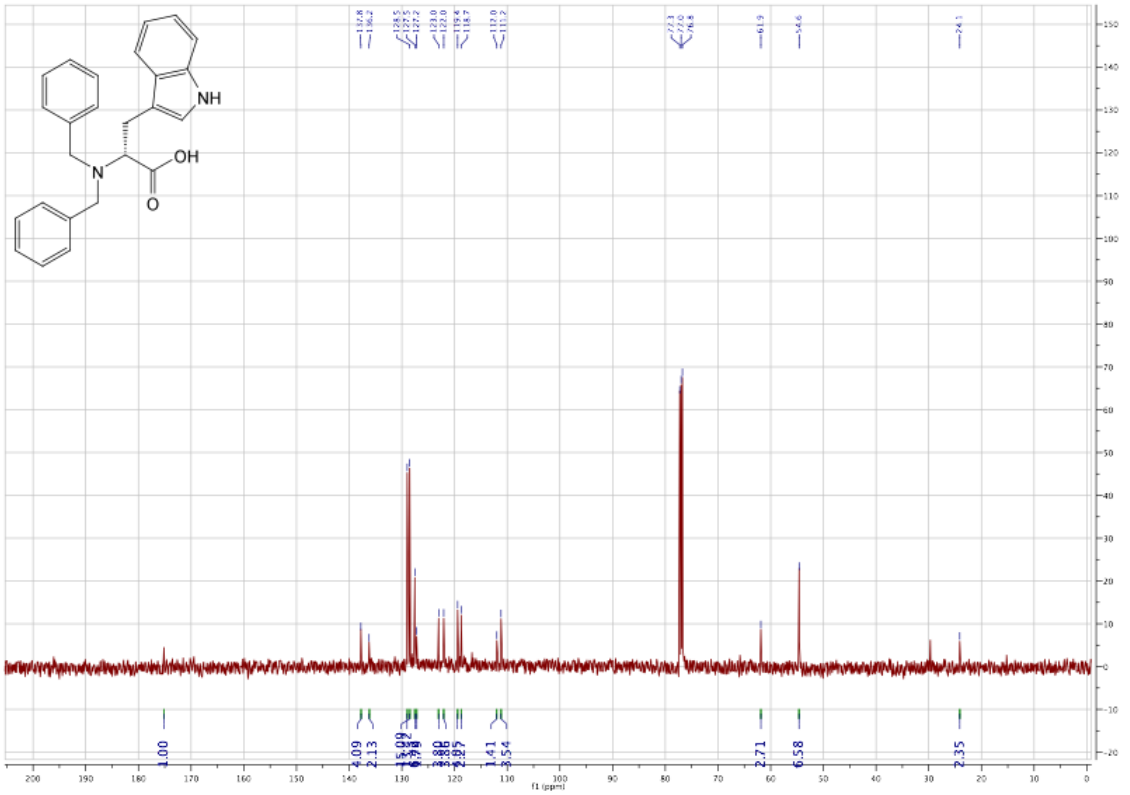
Triphenylphosphine gold N^2-[(benzyloxy)carbonyl}-N^1-[(trifluoromethyl)sulfonyl]-(*L*)-leucinamide (150)



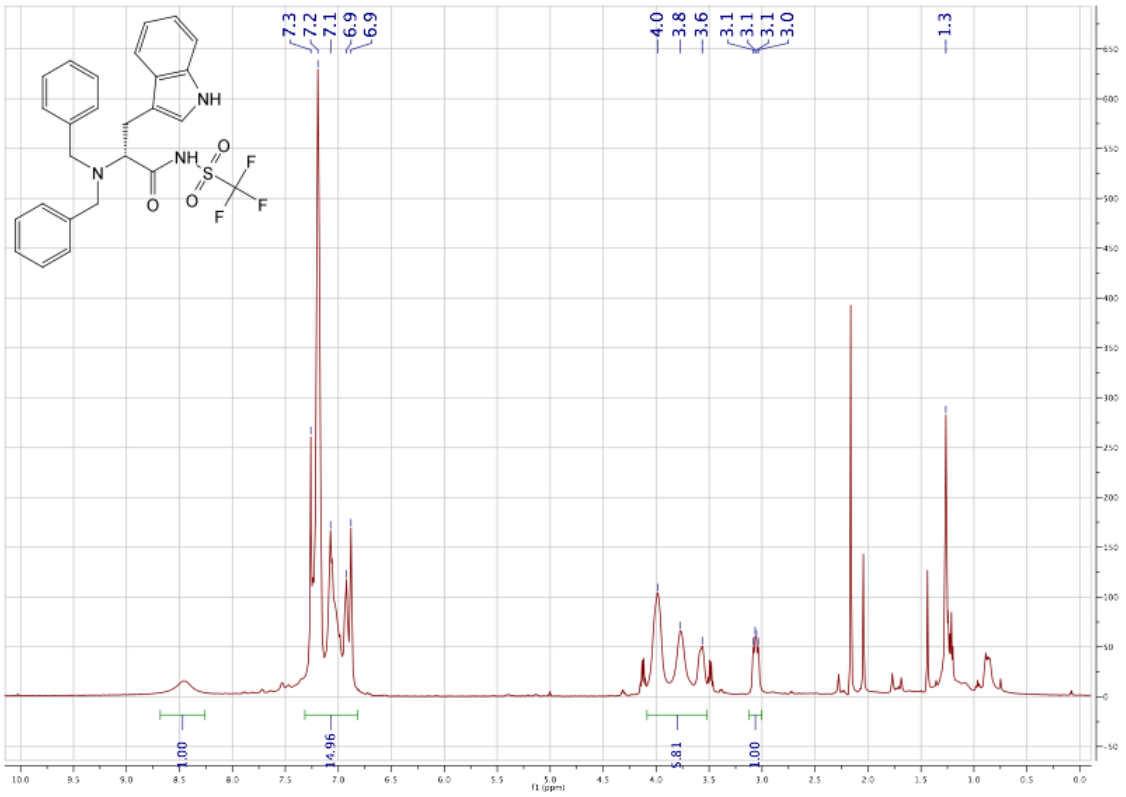


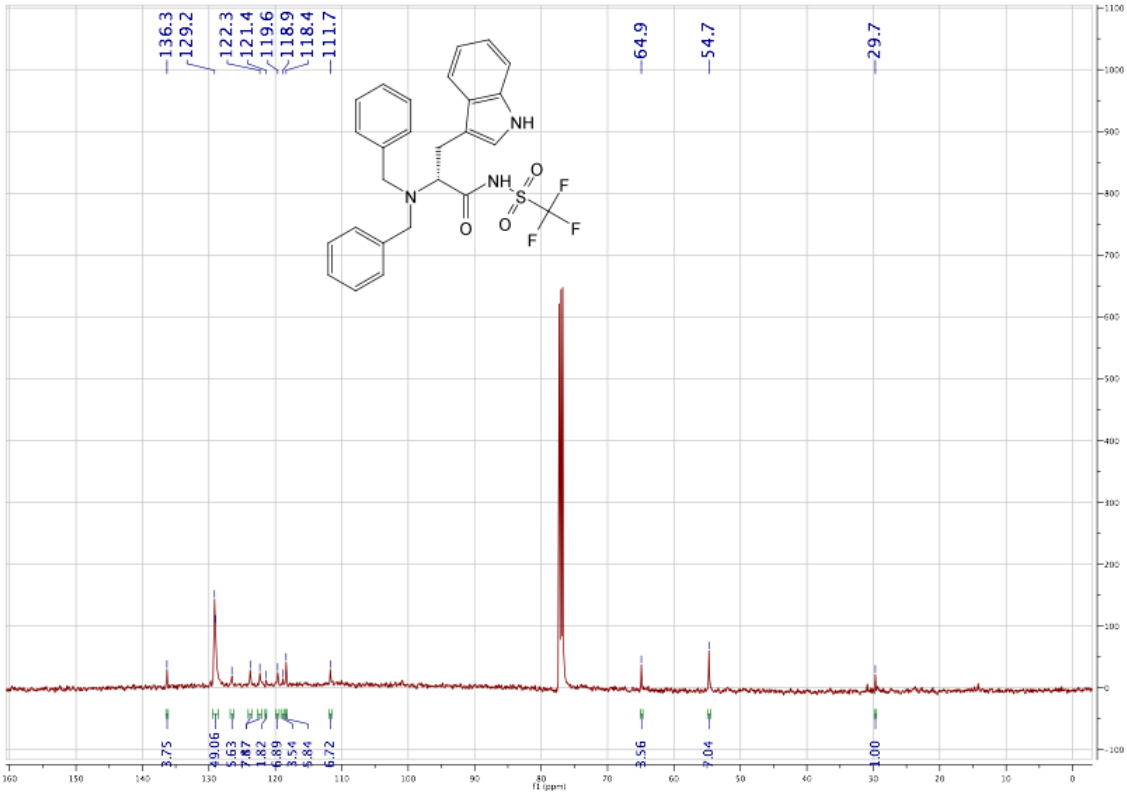
N,*N*-dibenzyl-(*D*)-tryptophan (154)



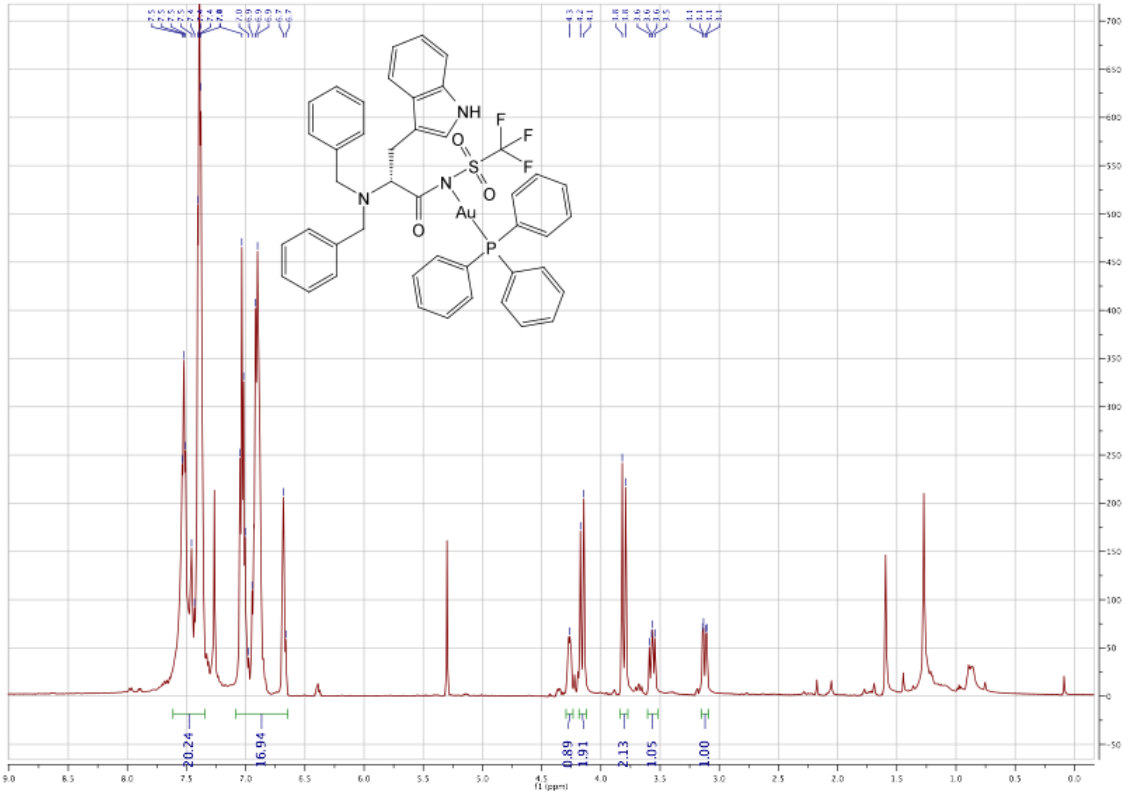


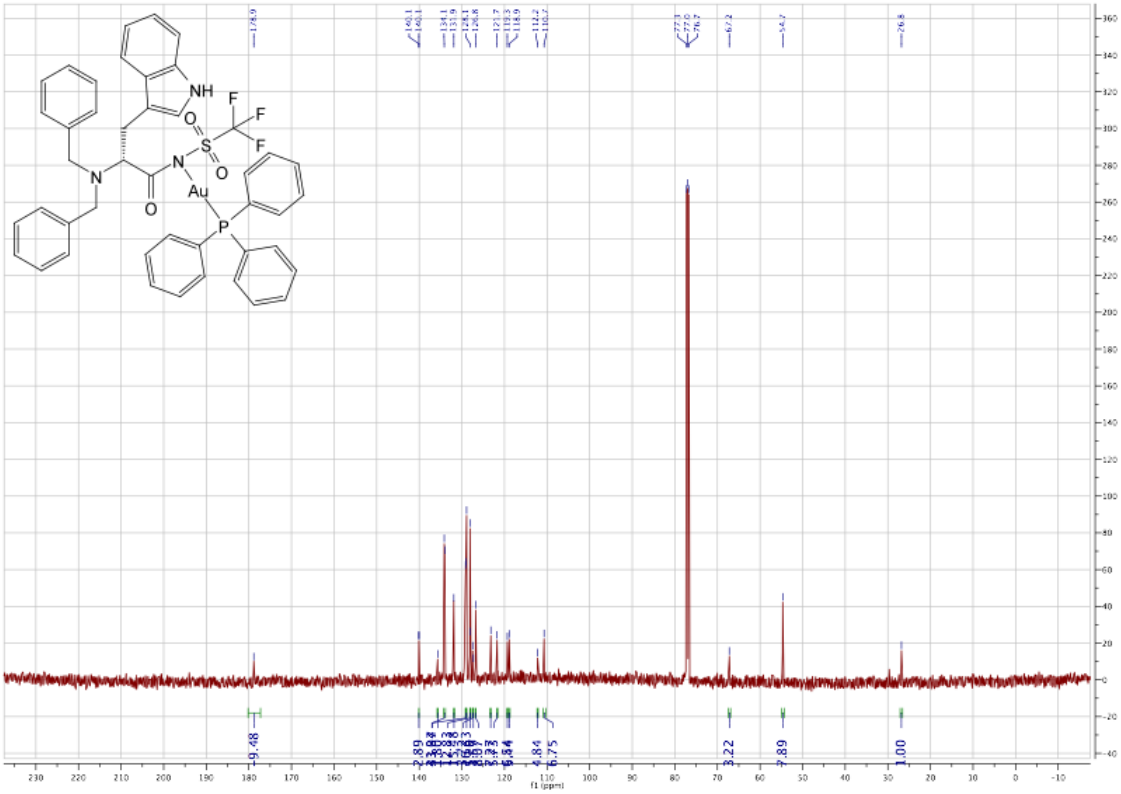
N,*N*-dibenzyl-*N*[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide (156)



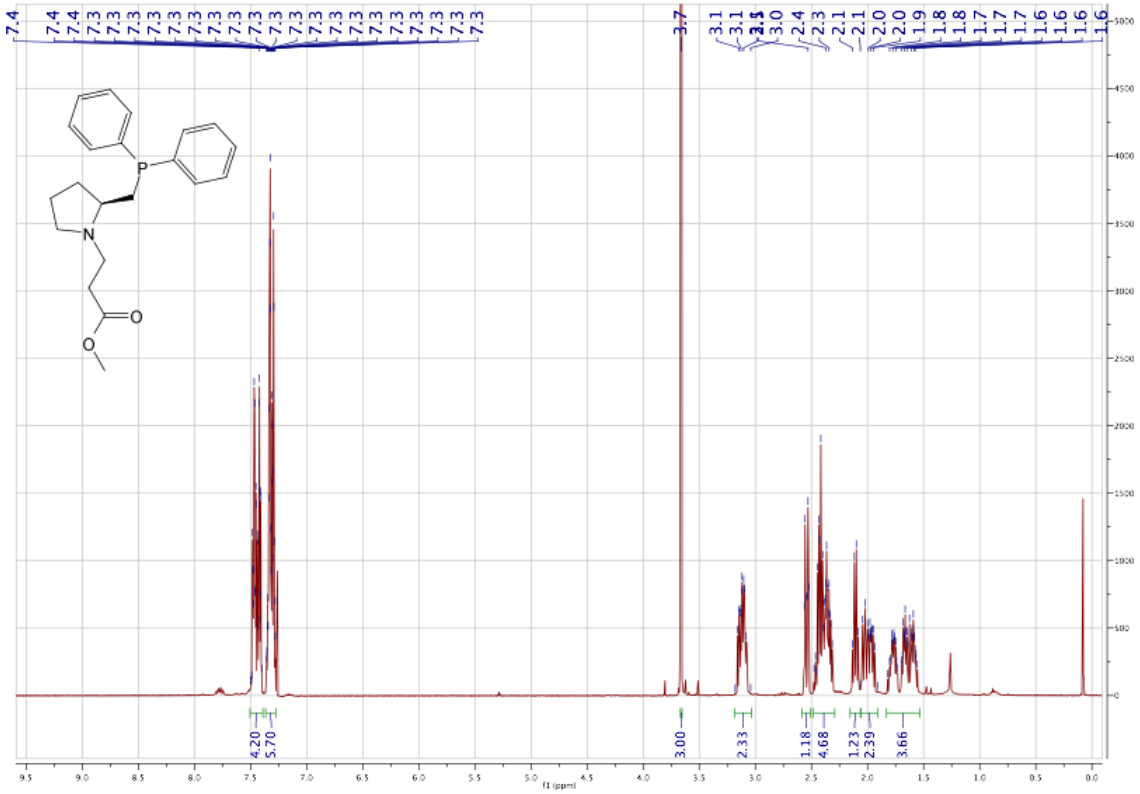


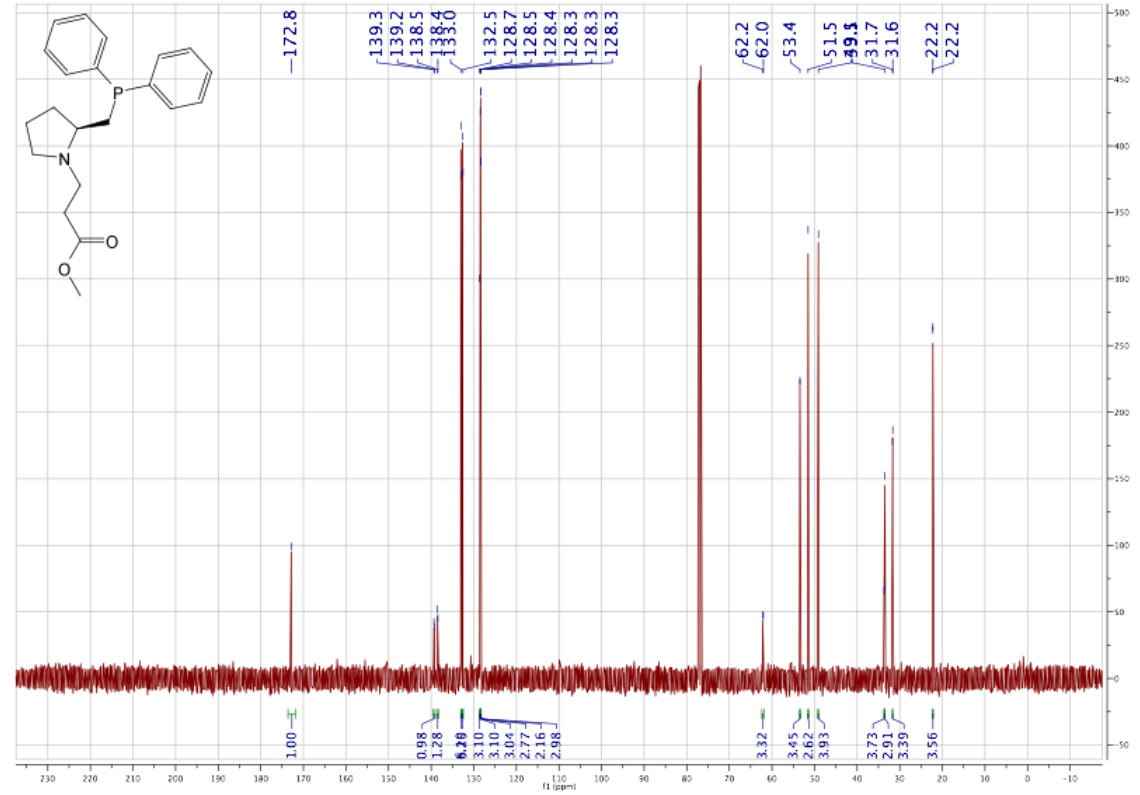
Triphenyphosphine gold *N*,*N*-dibenzyl-*N*[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide (157)



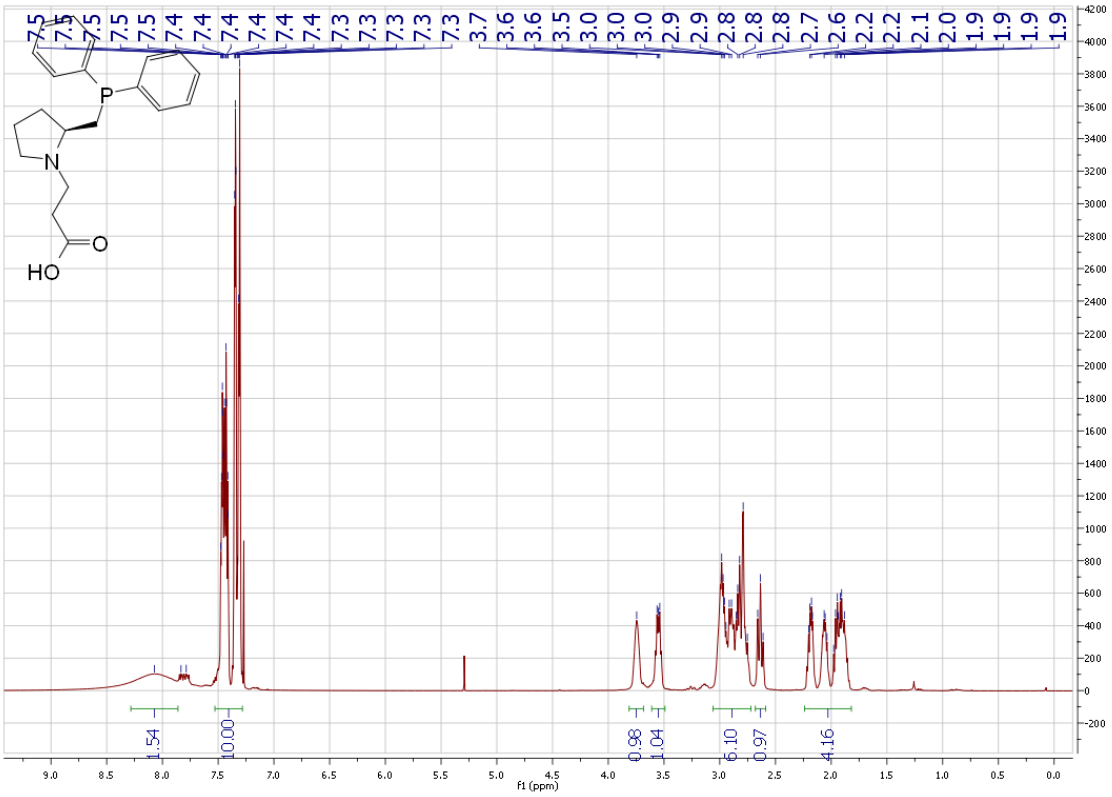


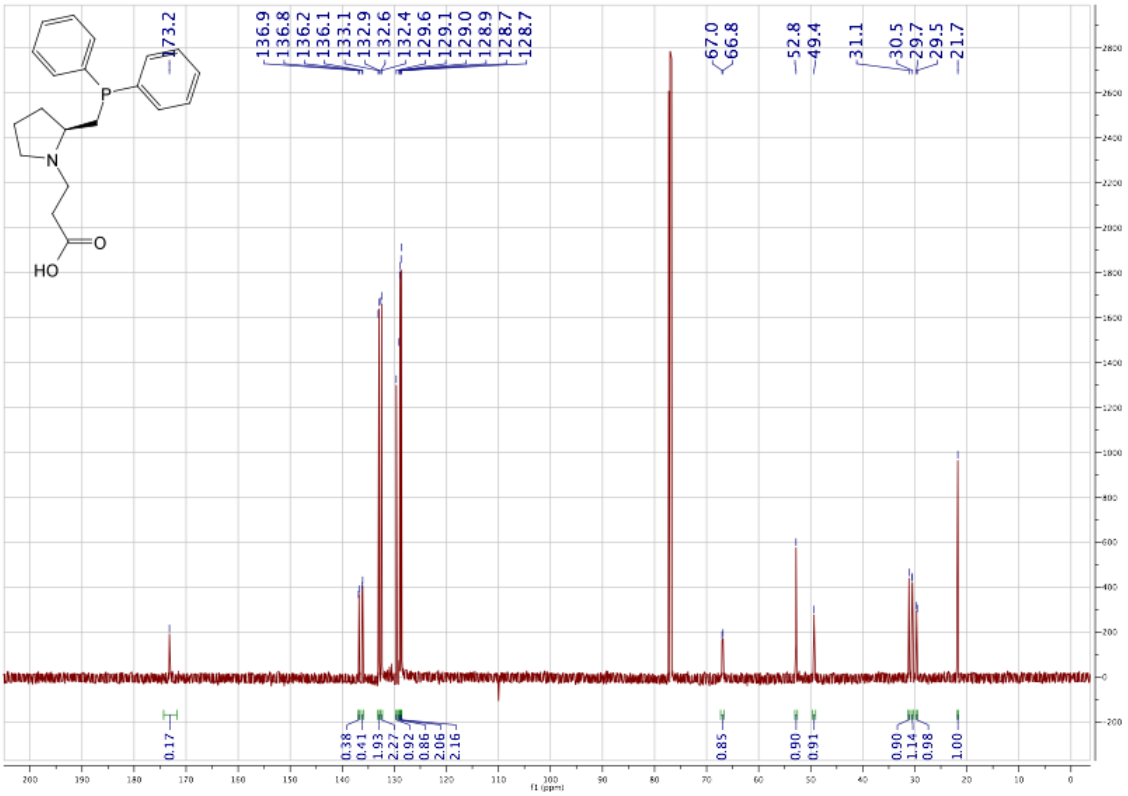
Methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl} propanoate (194)



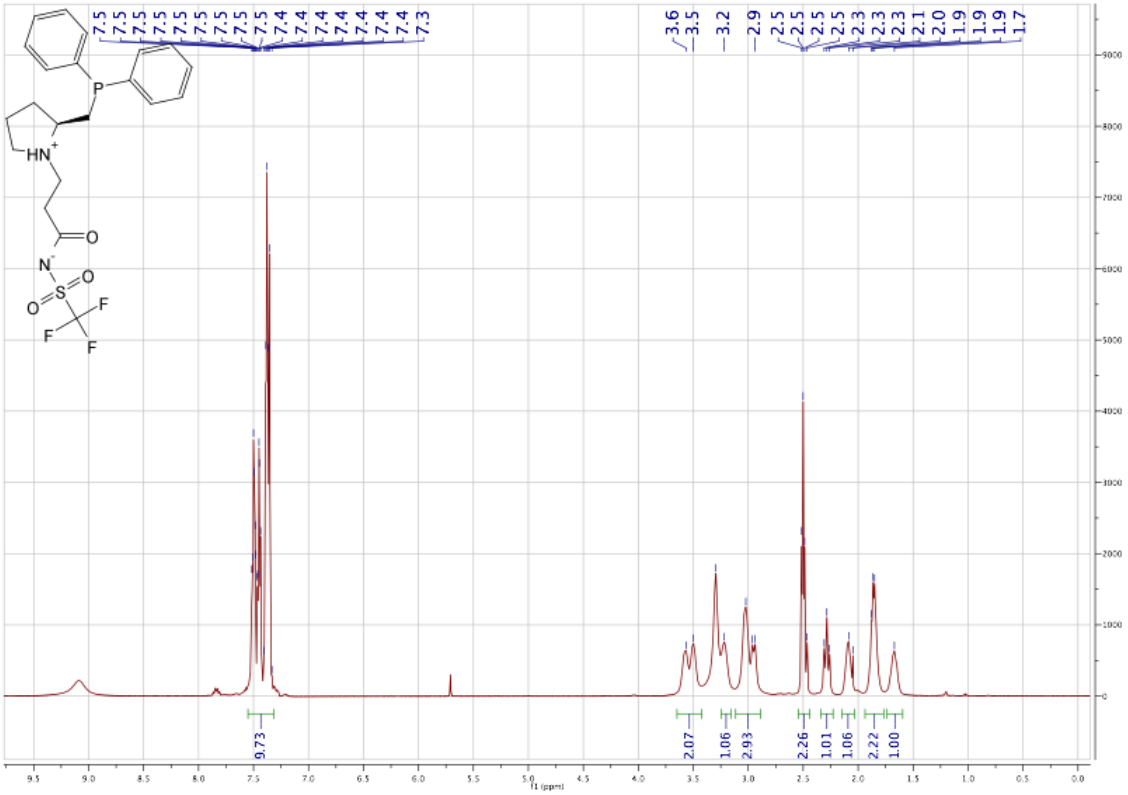


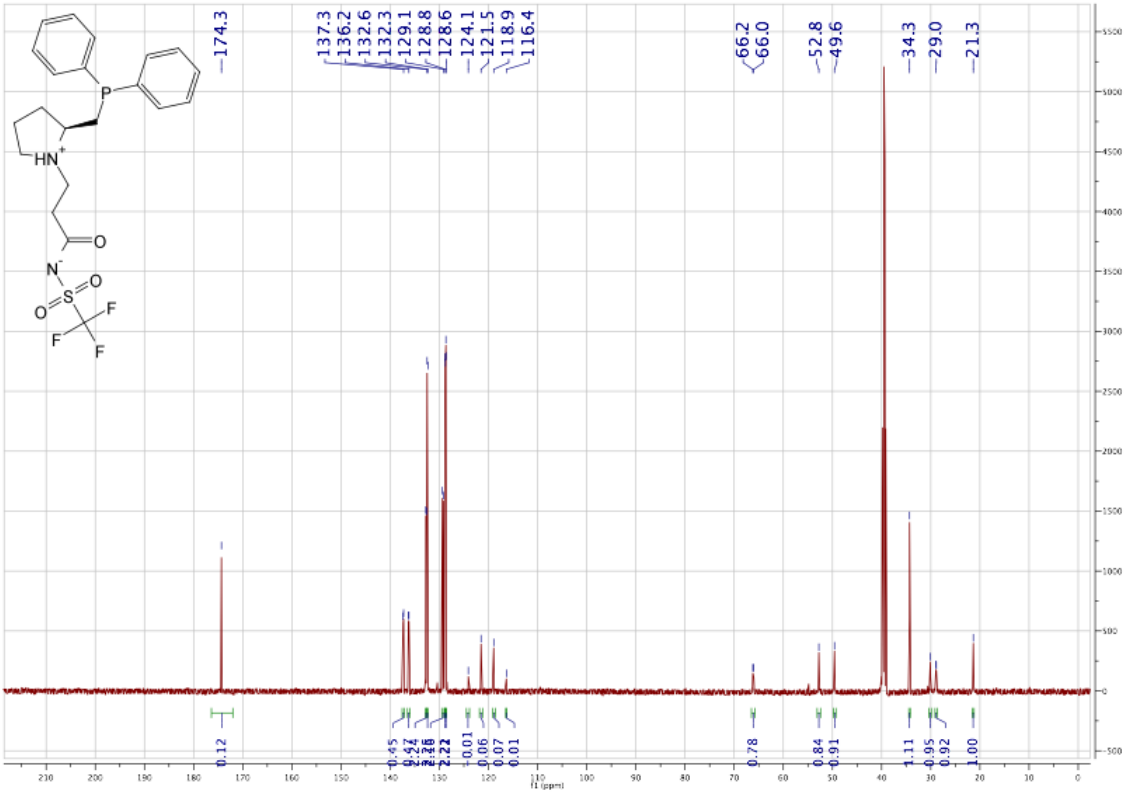
3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}propanoic acid (195)

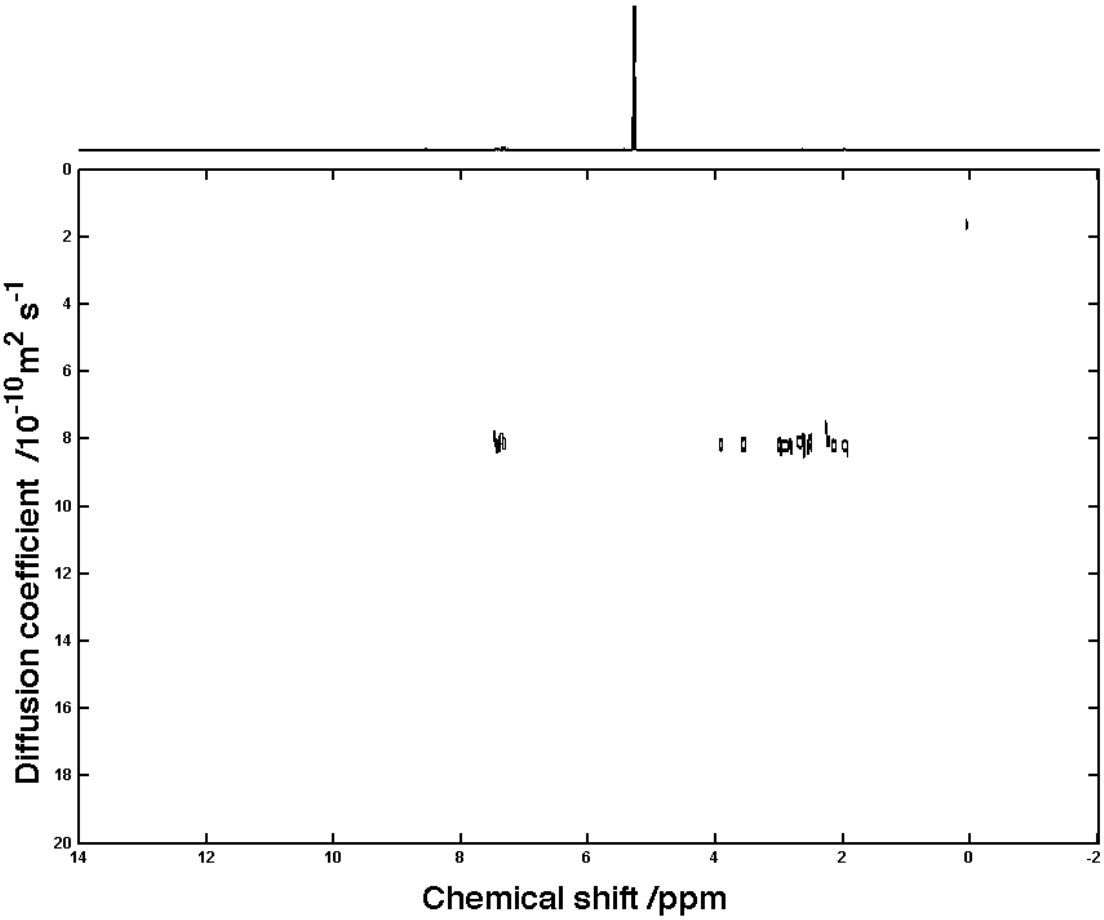




(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide (196)






Diffusion coefficient /10-10m2 s-1
0
2
4
6
8
10
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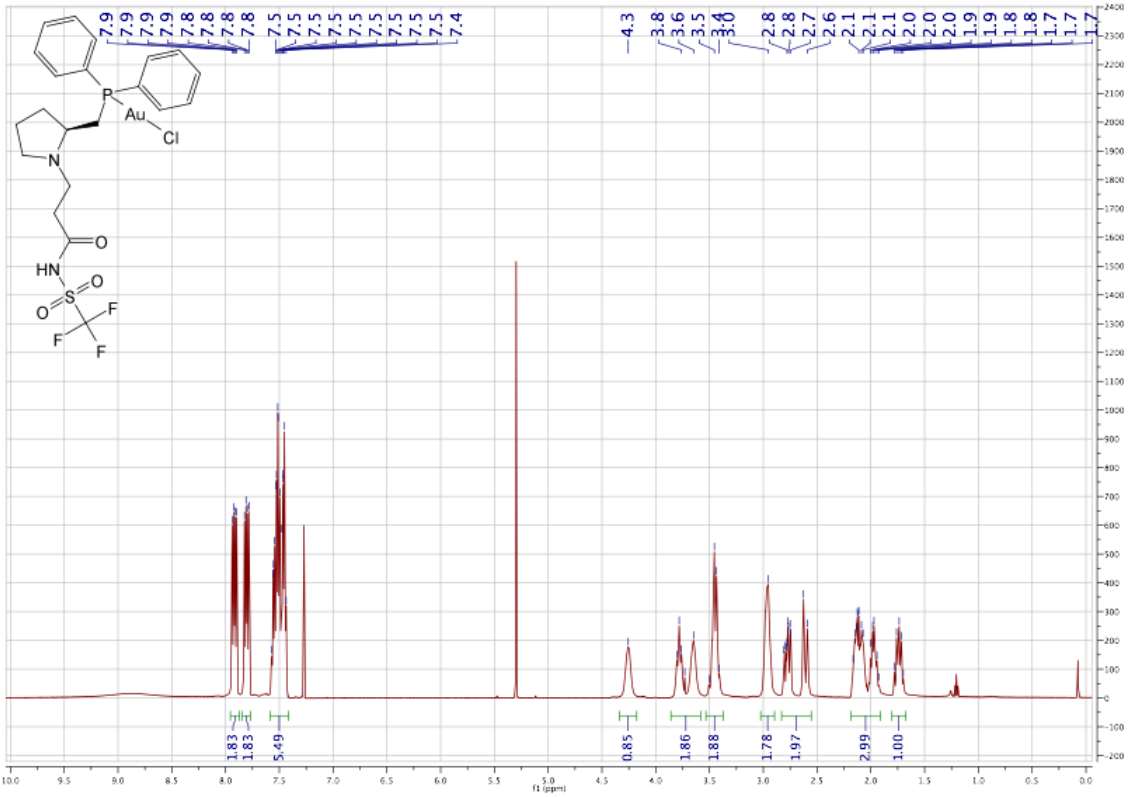
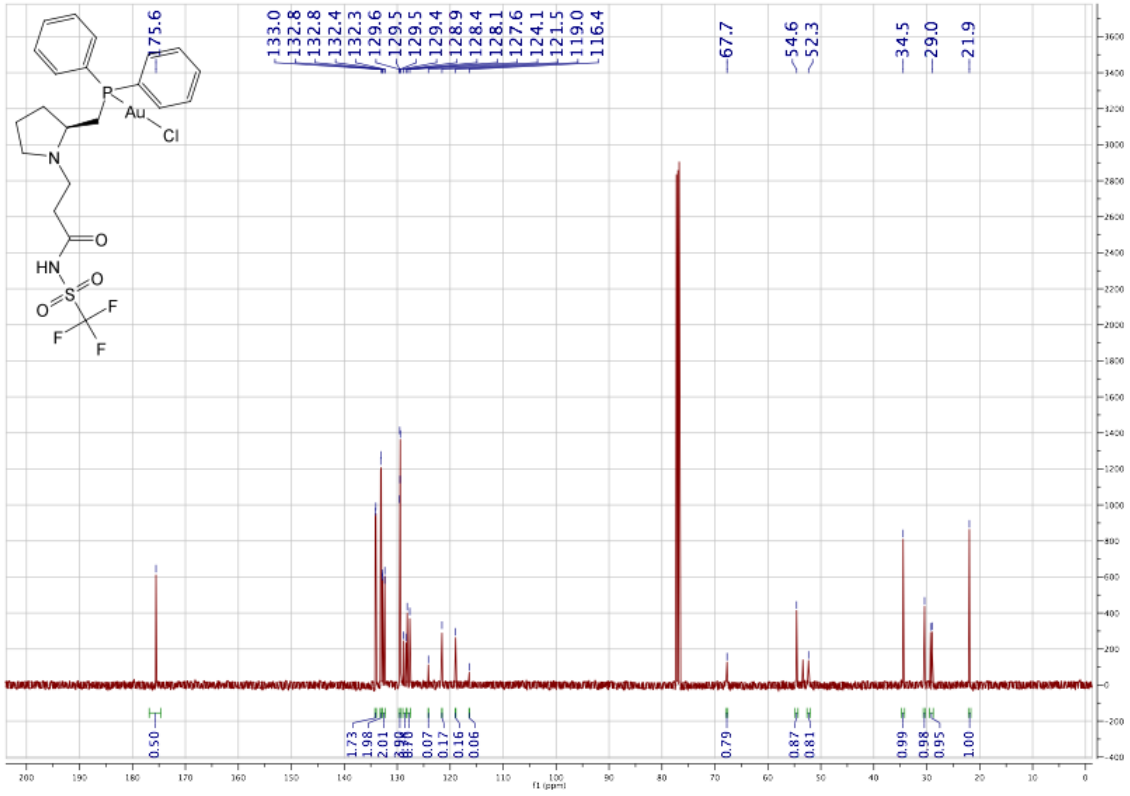
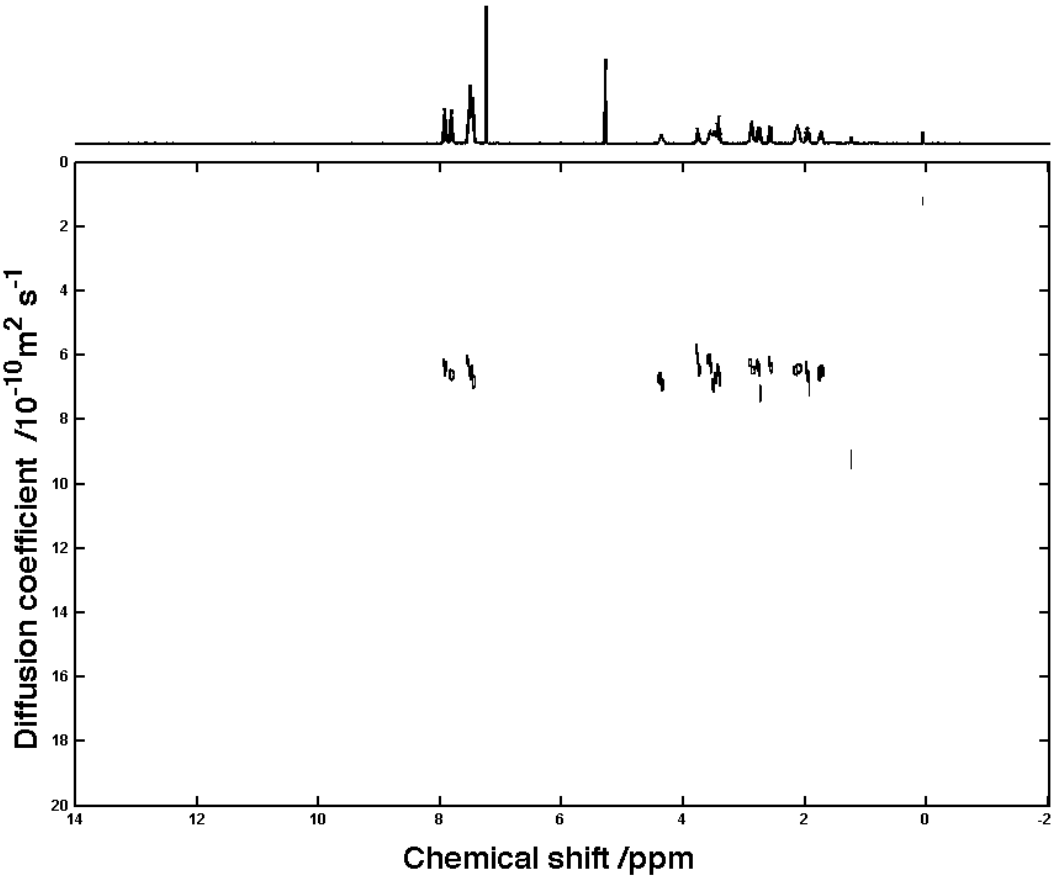
10
8
6
4
2
0
-2
Chemical shift /ppm

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide gold chloride (198)






Diffusion coefficient /10-10m2 s-1
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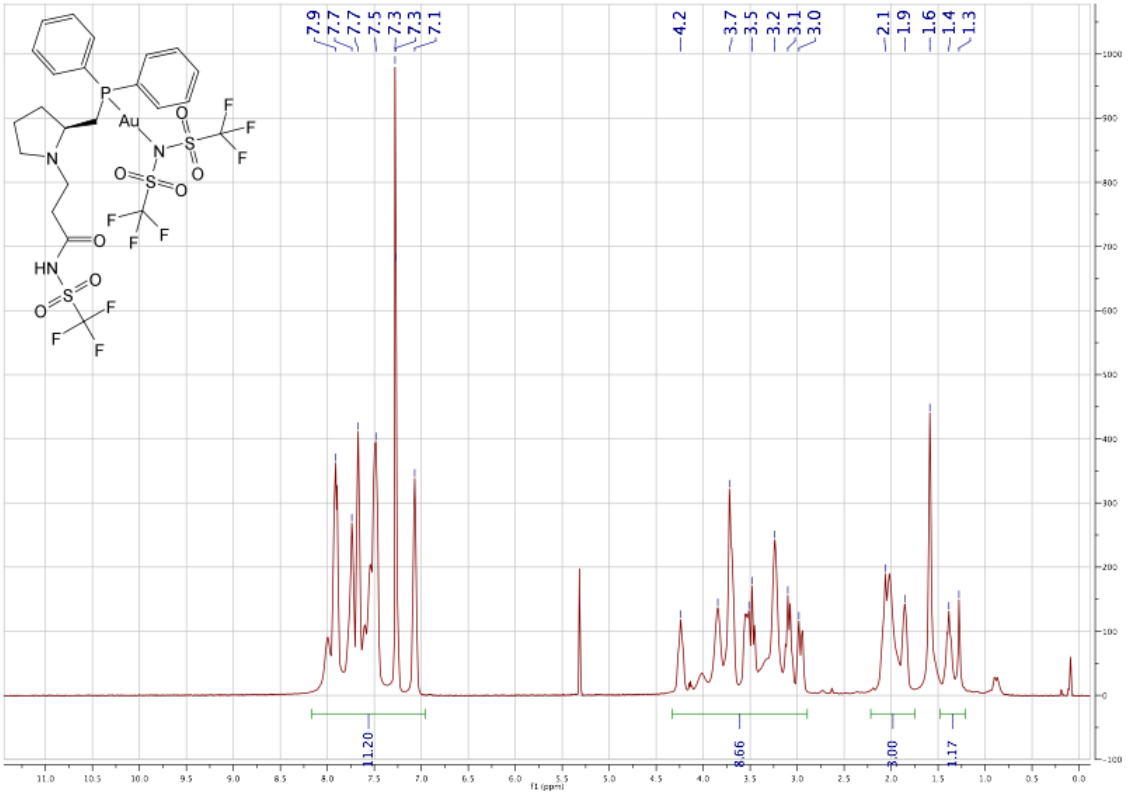
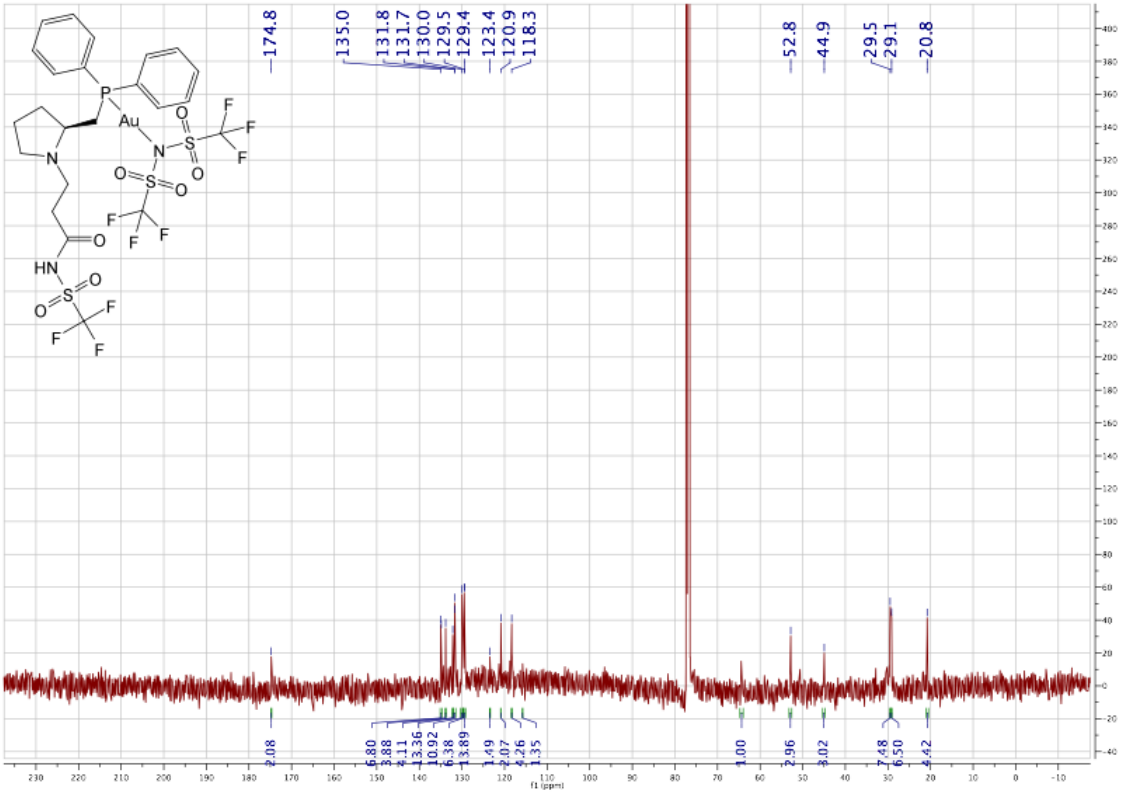
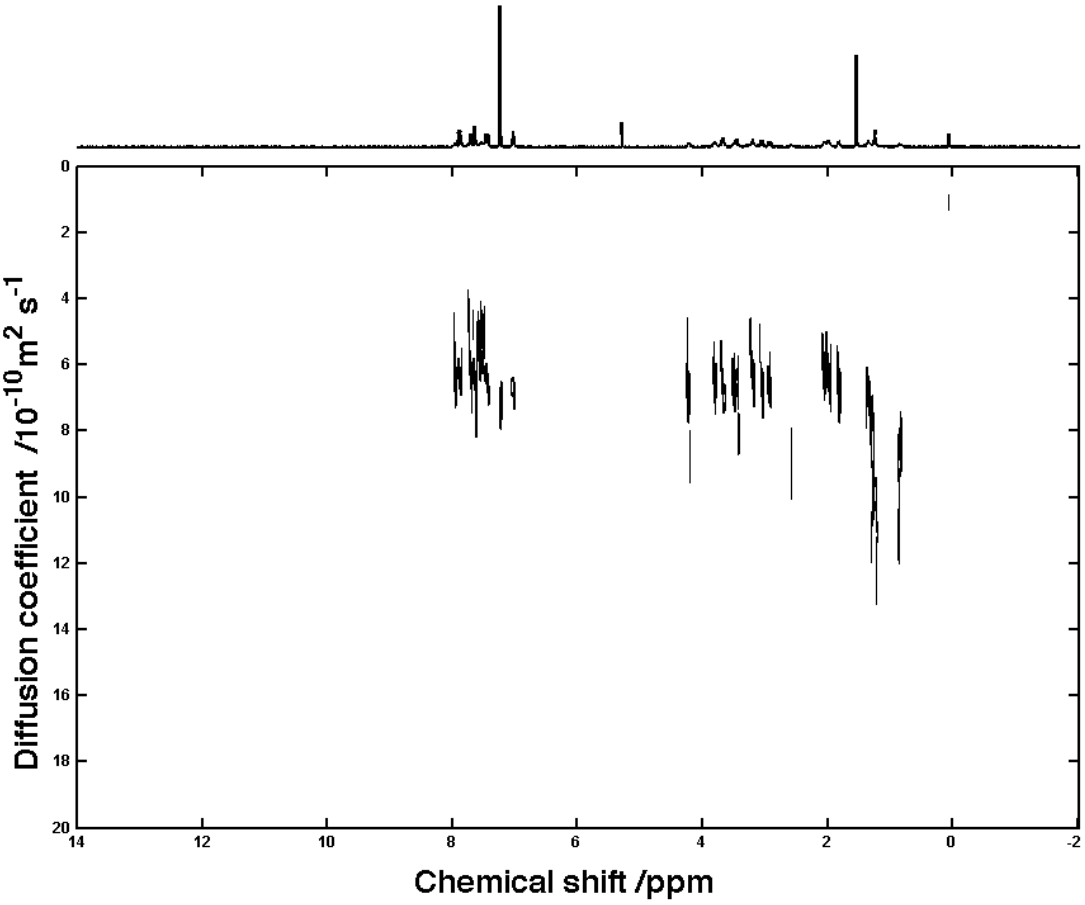
2
0
-2
Chemical shift /ppm

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide gold bistriflic amide (199)






Diffusion coefficient /10^-10 m^2 s^-1
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18
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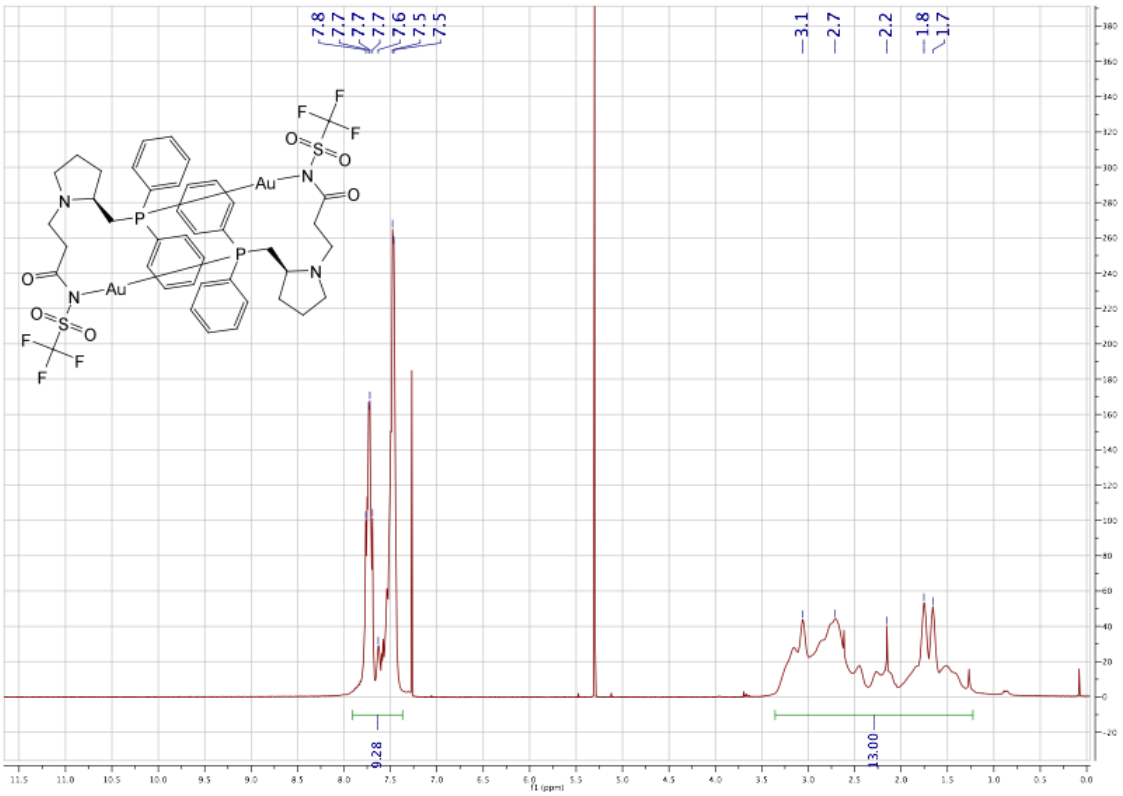
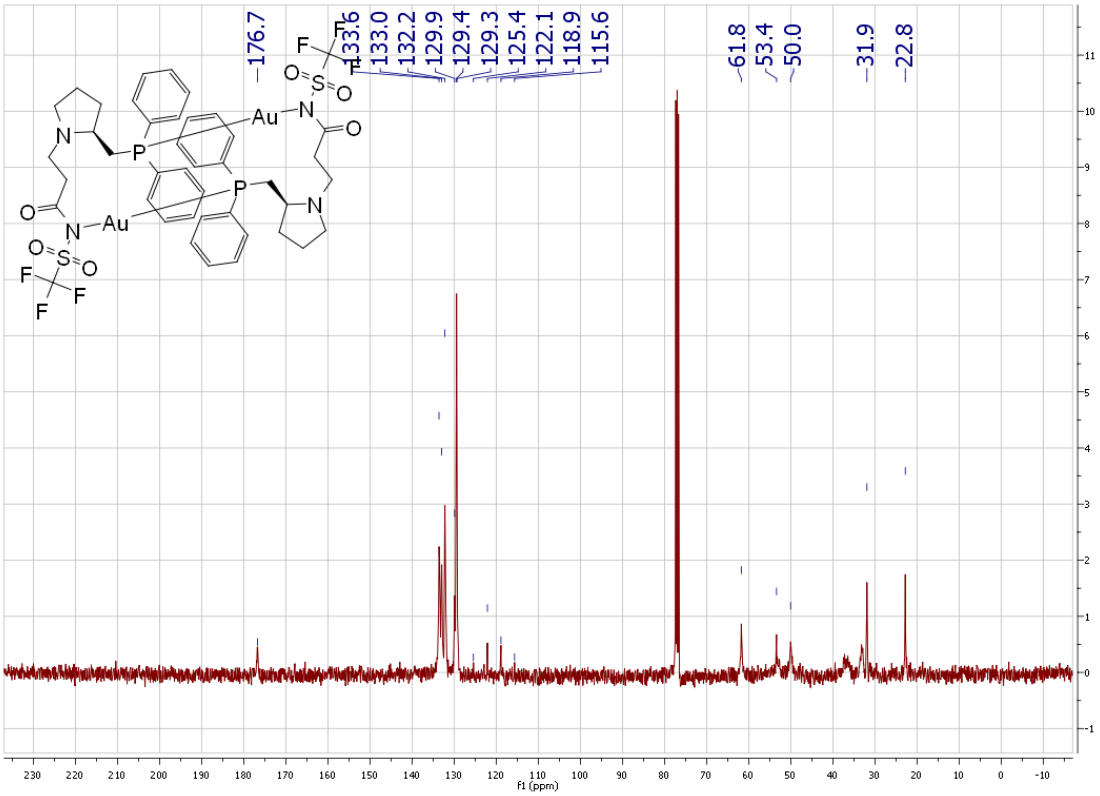
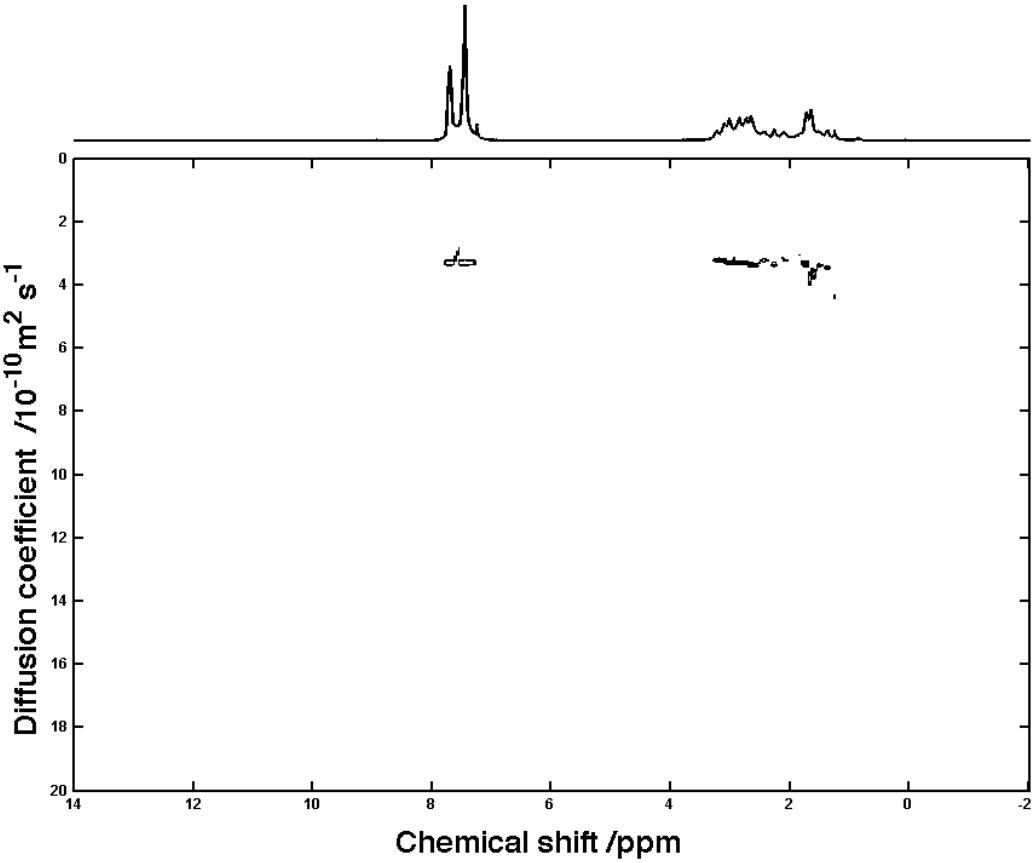
8
6
4
2
0
-2
Chemical shift /ppm

Bidentate gold(I) complex – dimer (197)






Diffusion coefficient /10-10m2 s-1
0
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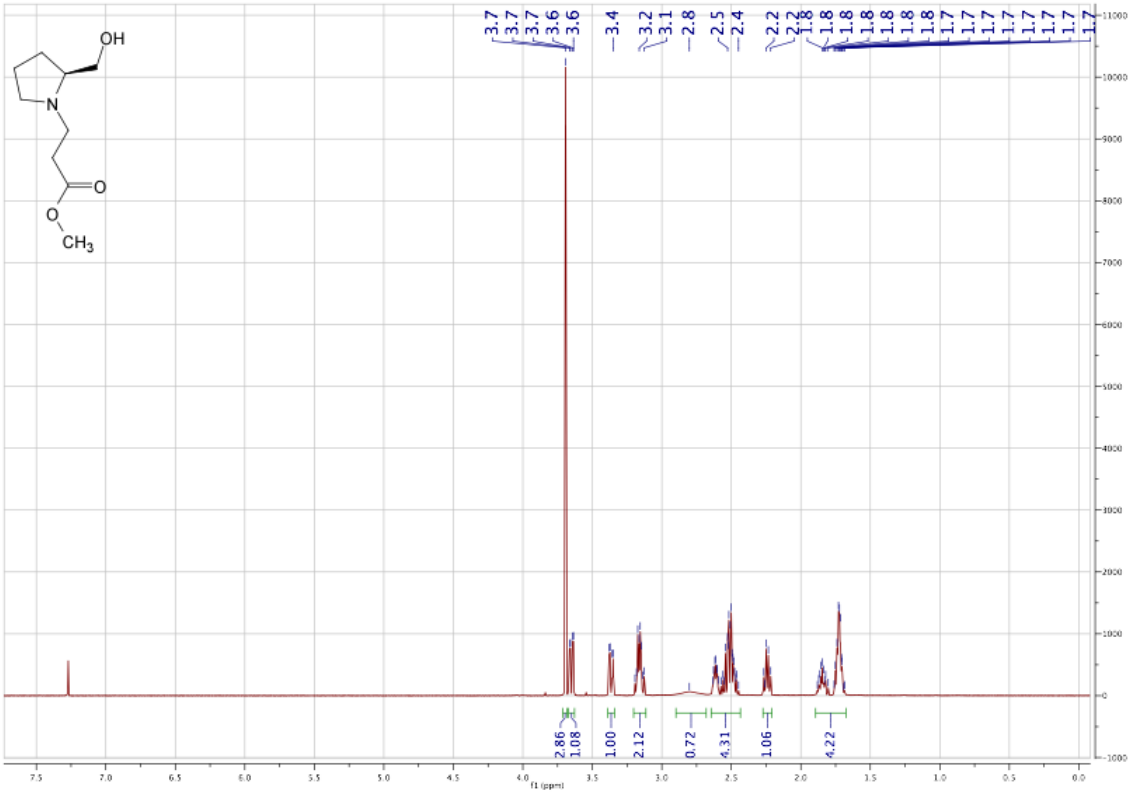
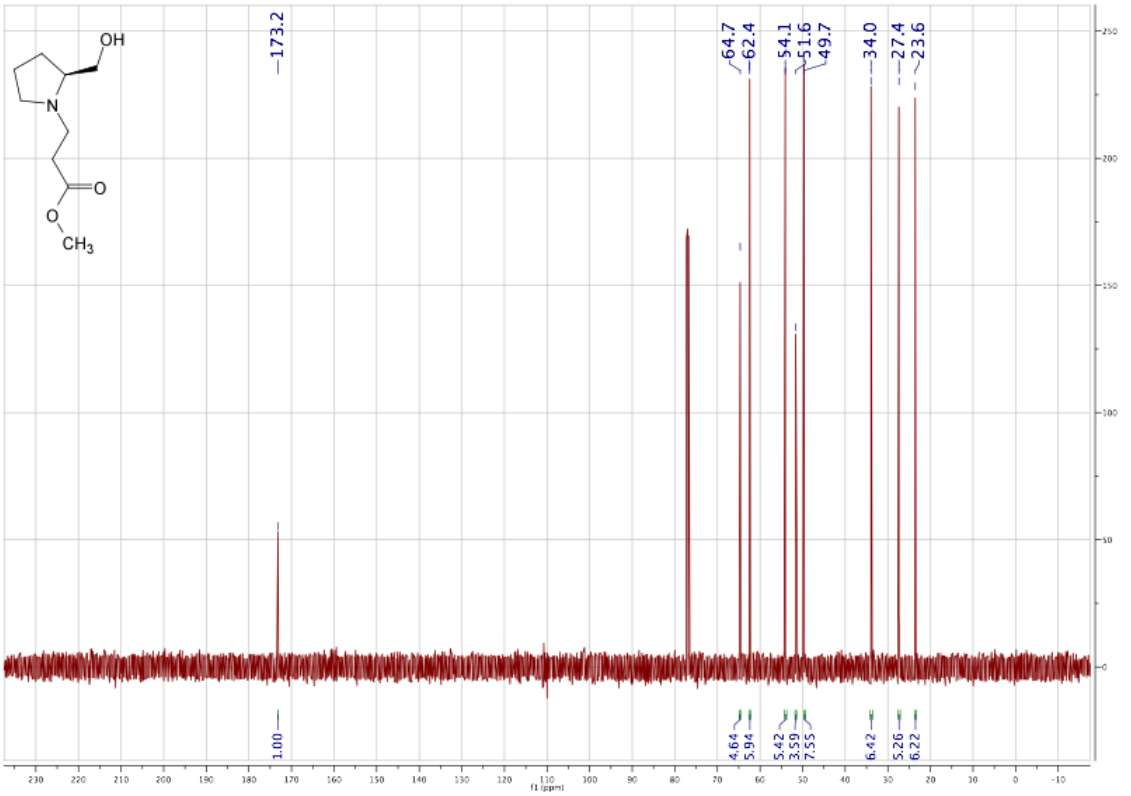
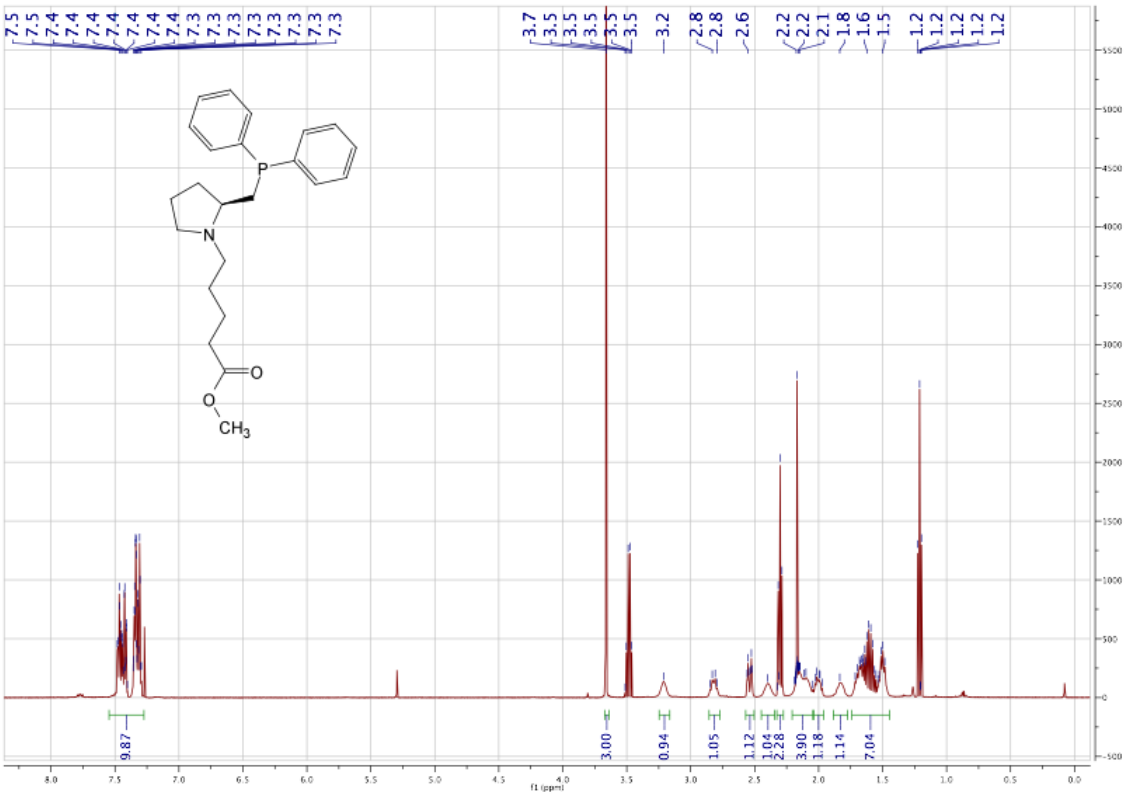
6
4
2
0
-2
Chemical shift /ppm

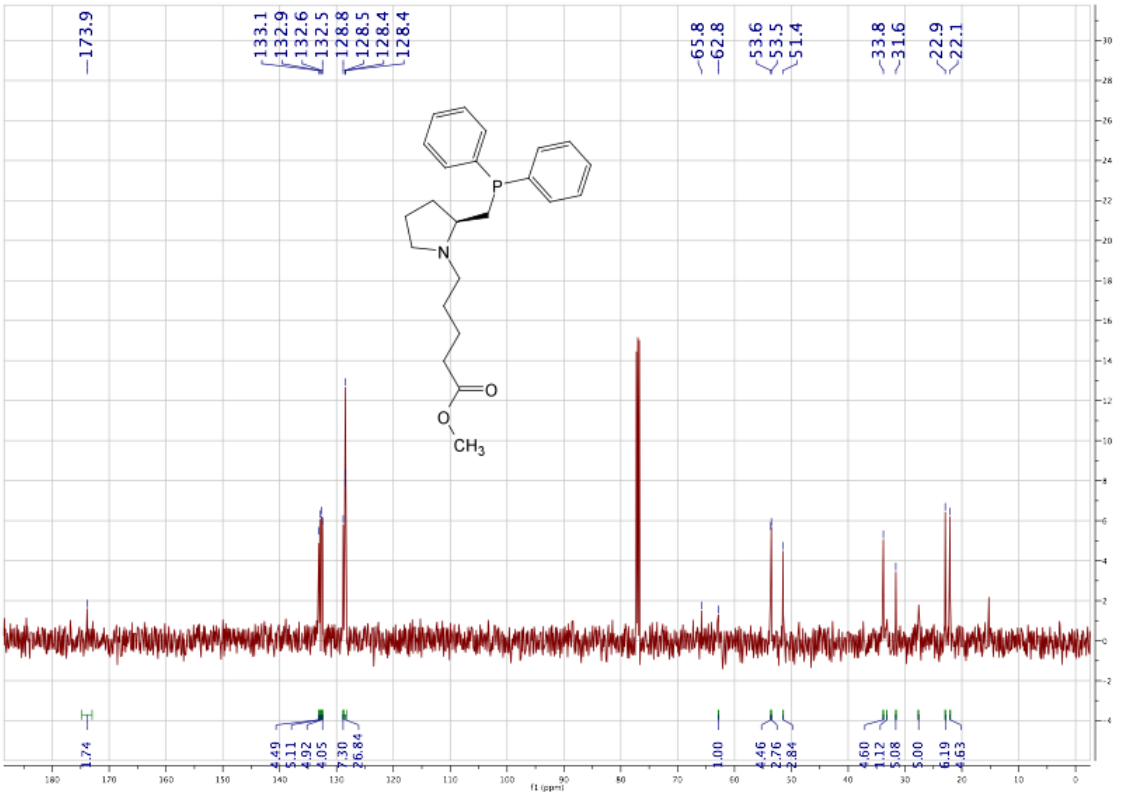
Methyl 3-[(2*S*)-2-(hydroxymethyl)pyrrolidin-1-yl]propanoate (192)



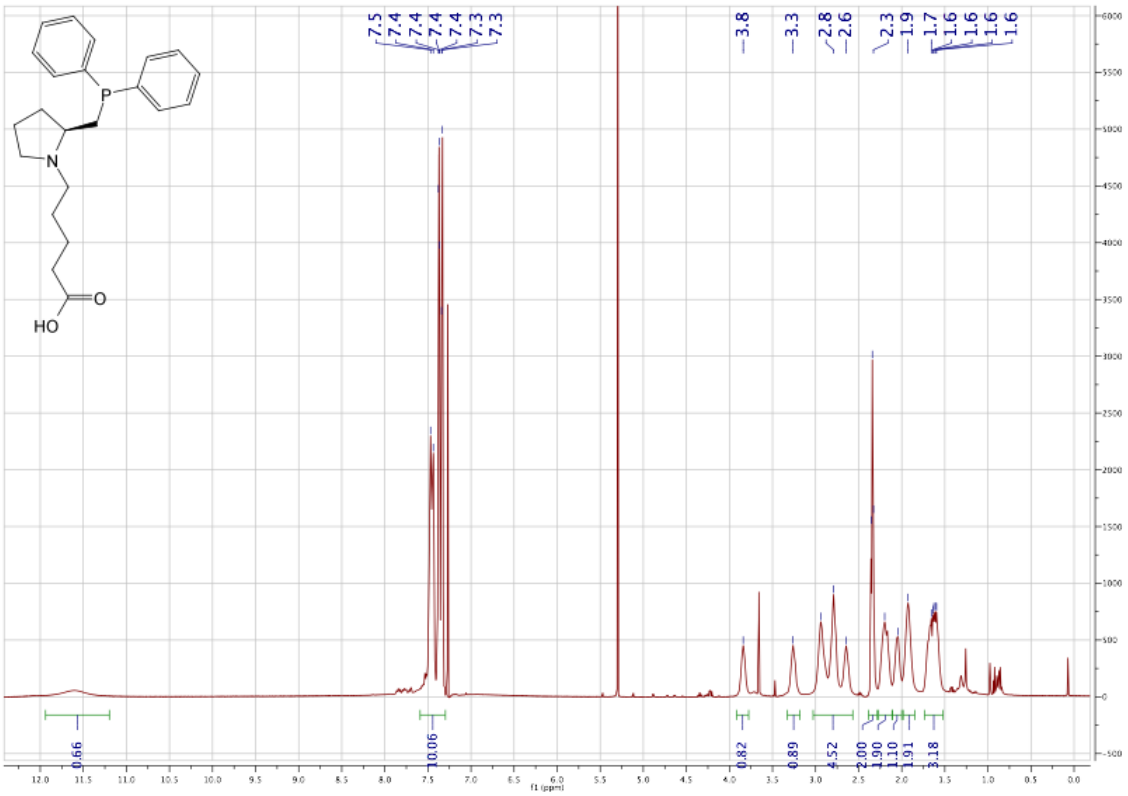


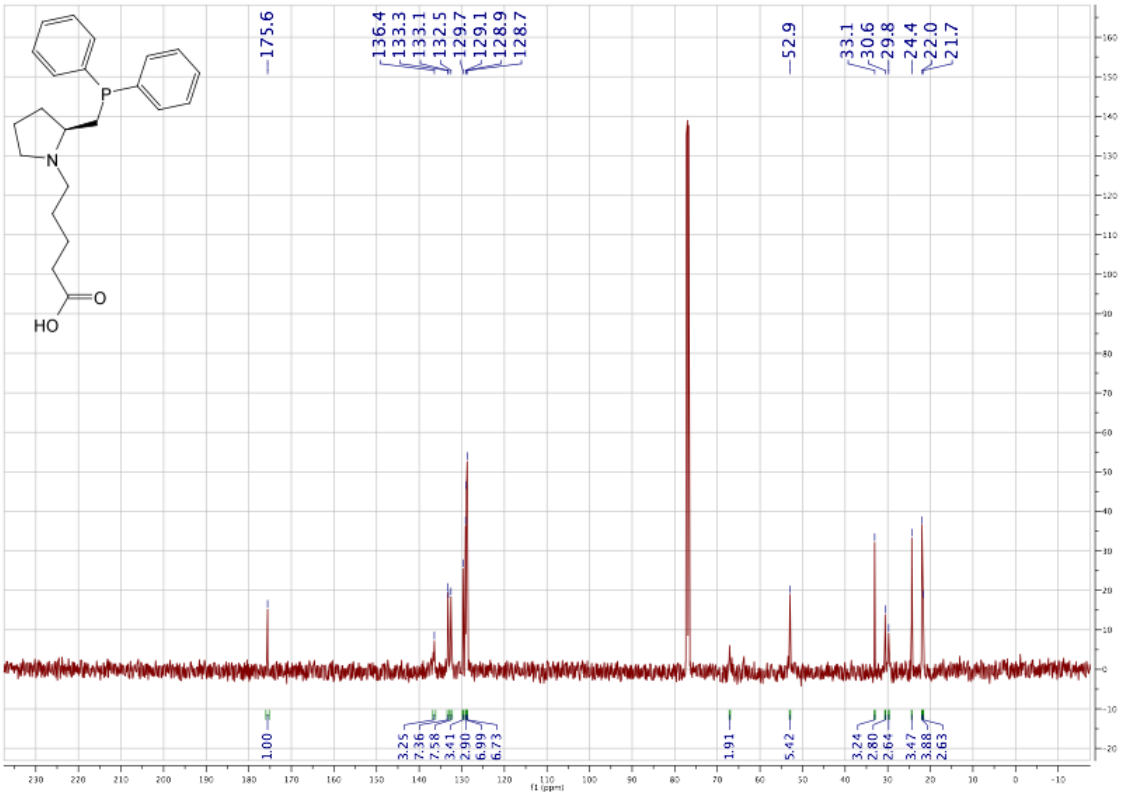
(*S*)-methyl 5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoate (200)



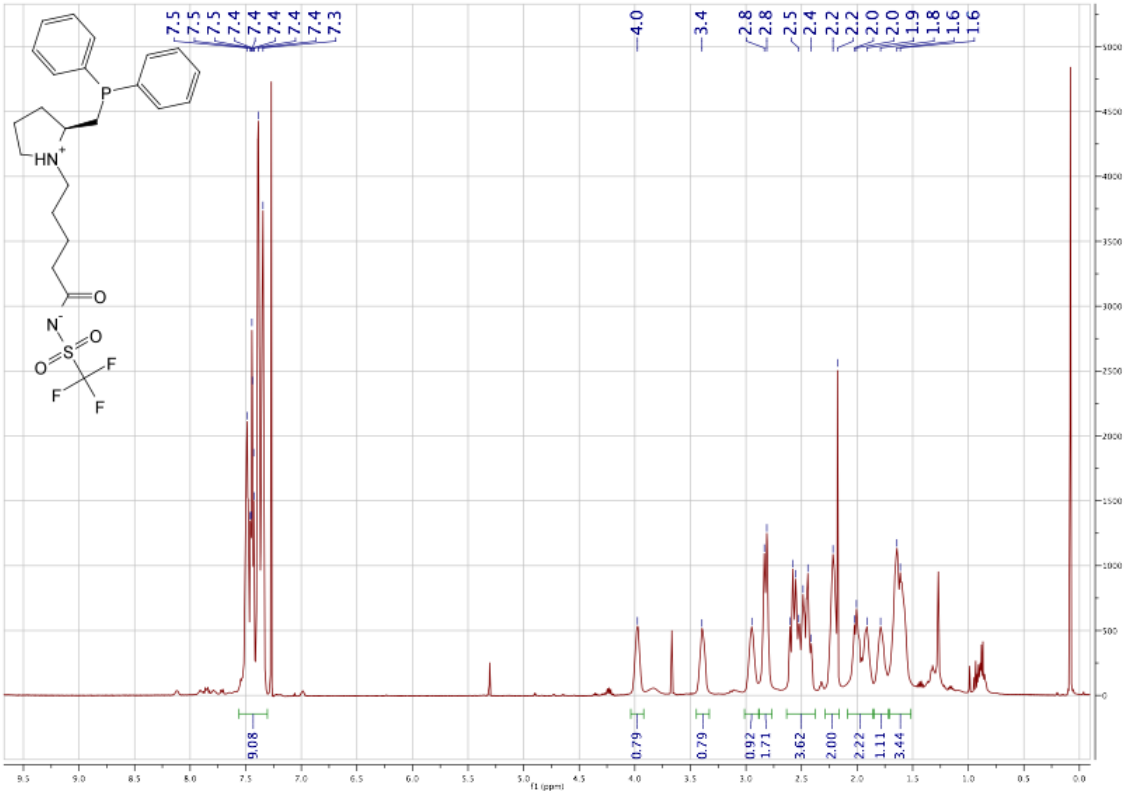


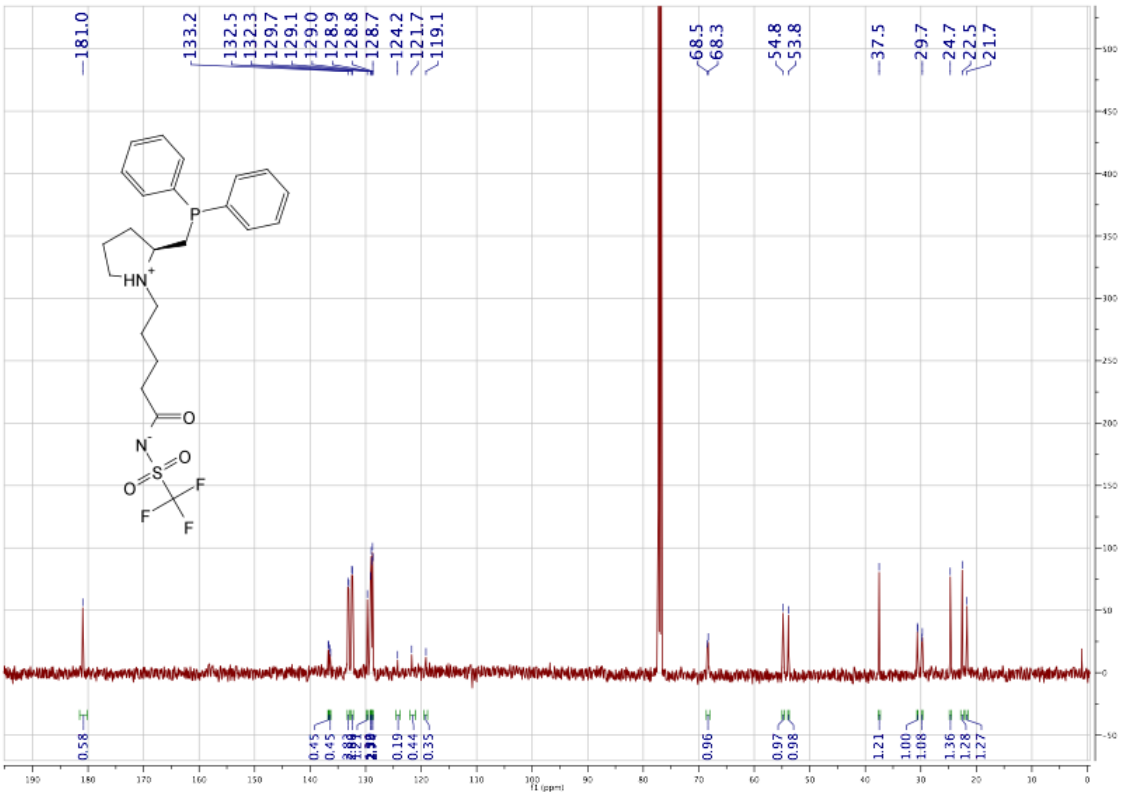
(*S*)-5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoic acid (204)

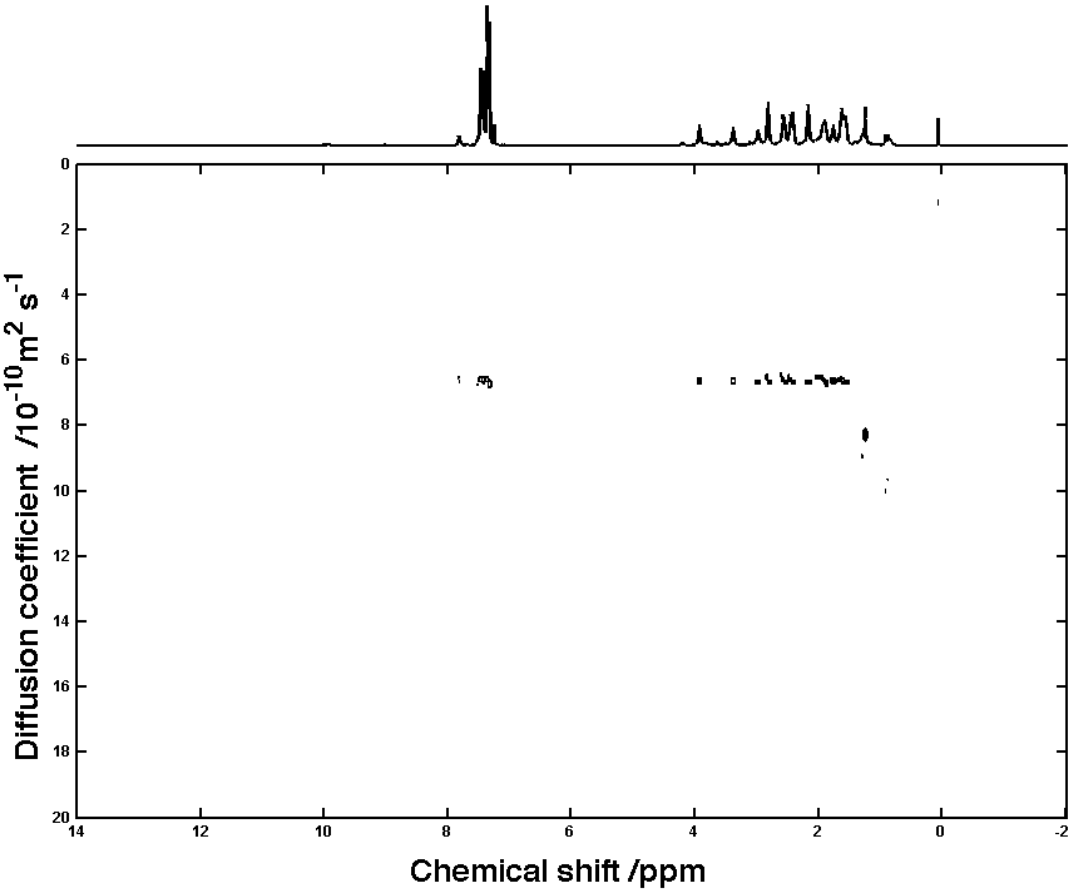




(5-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)pentanoyl)((trifluoromethyl)sulfonyl)amide (206)






Diffusion coefficient /10-10m2 s-1
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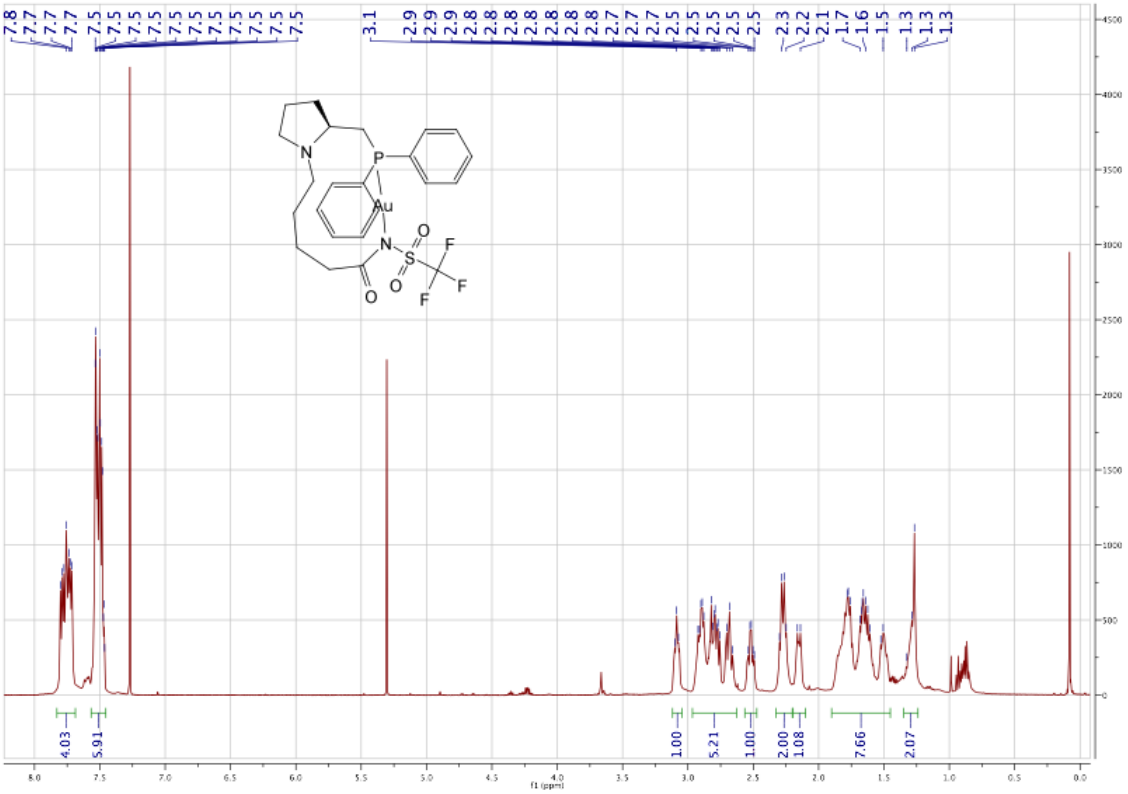
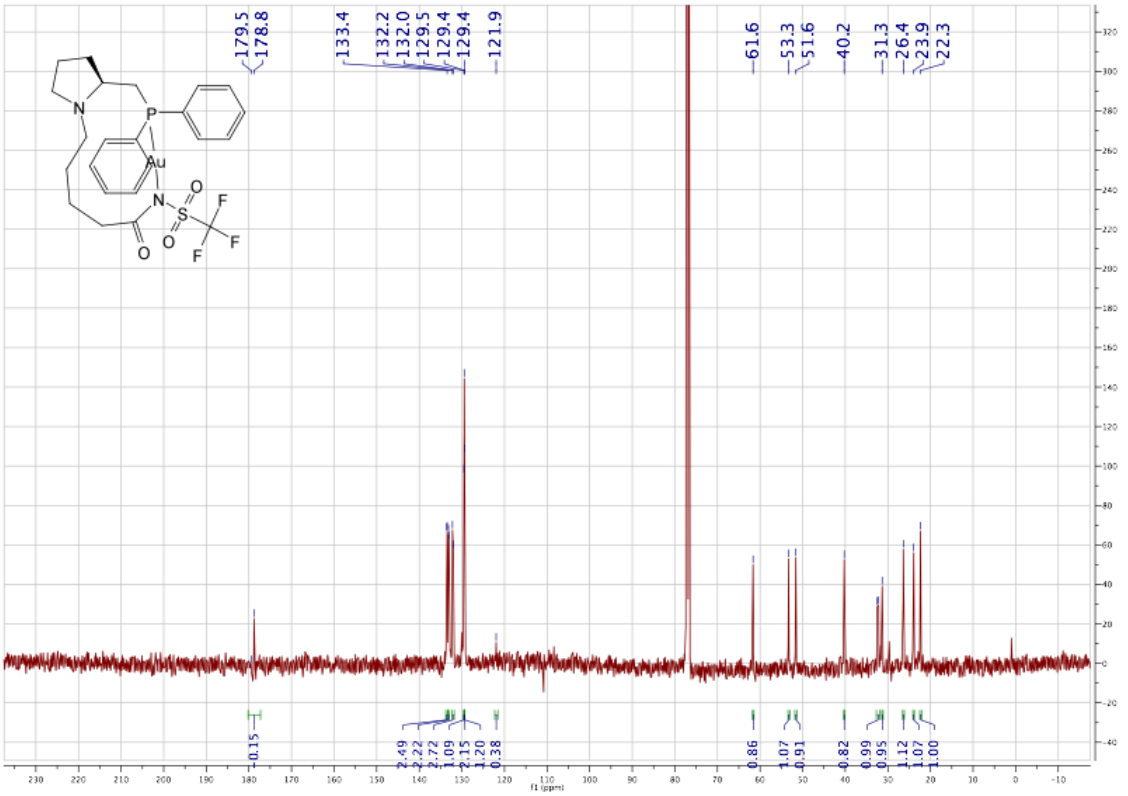
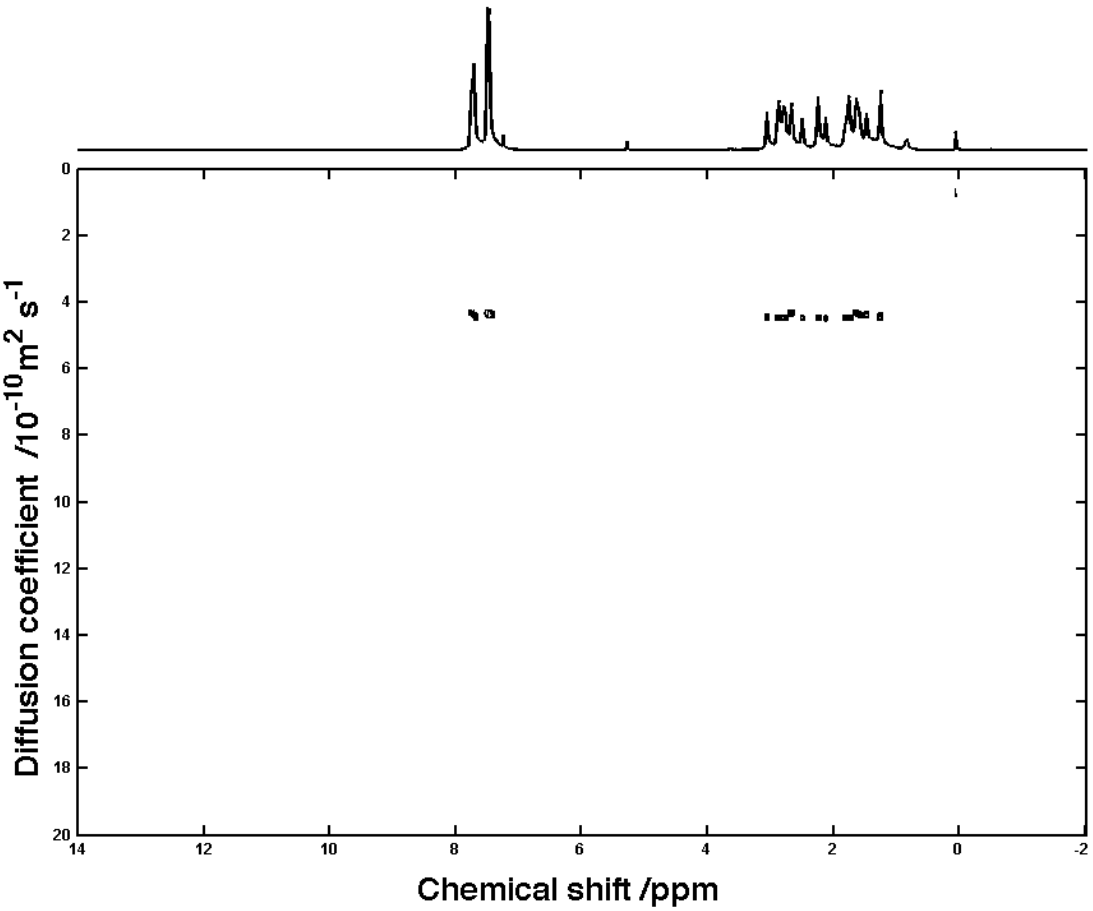
-2
Chemical shift /ppm

Bidentate gold(I) complex – monomer (207)






Diffusion coefficient /10^-10 m^2 s^-1
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2
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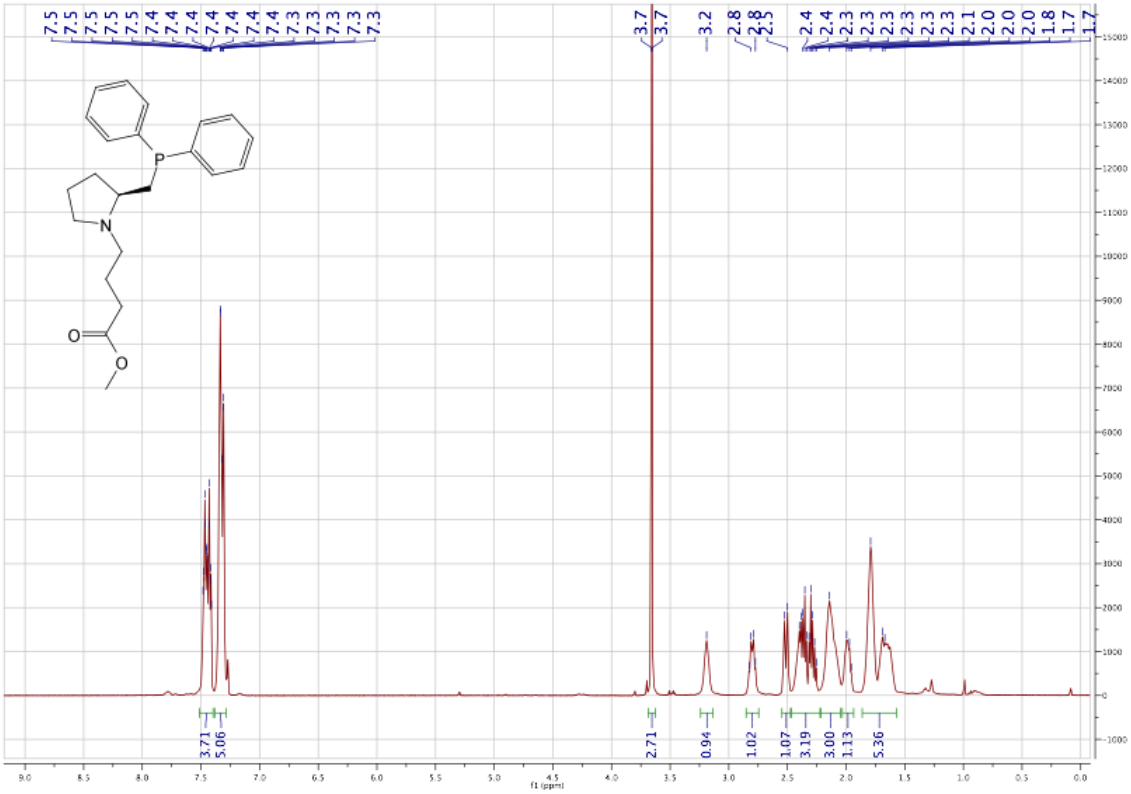
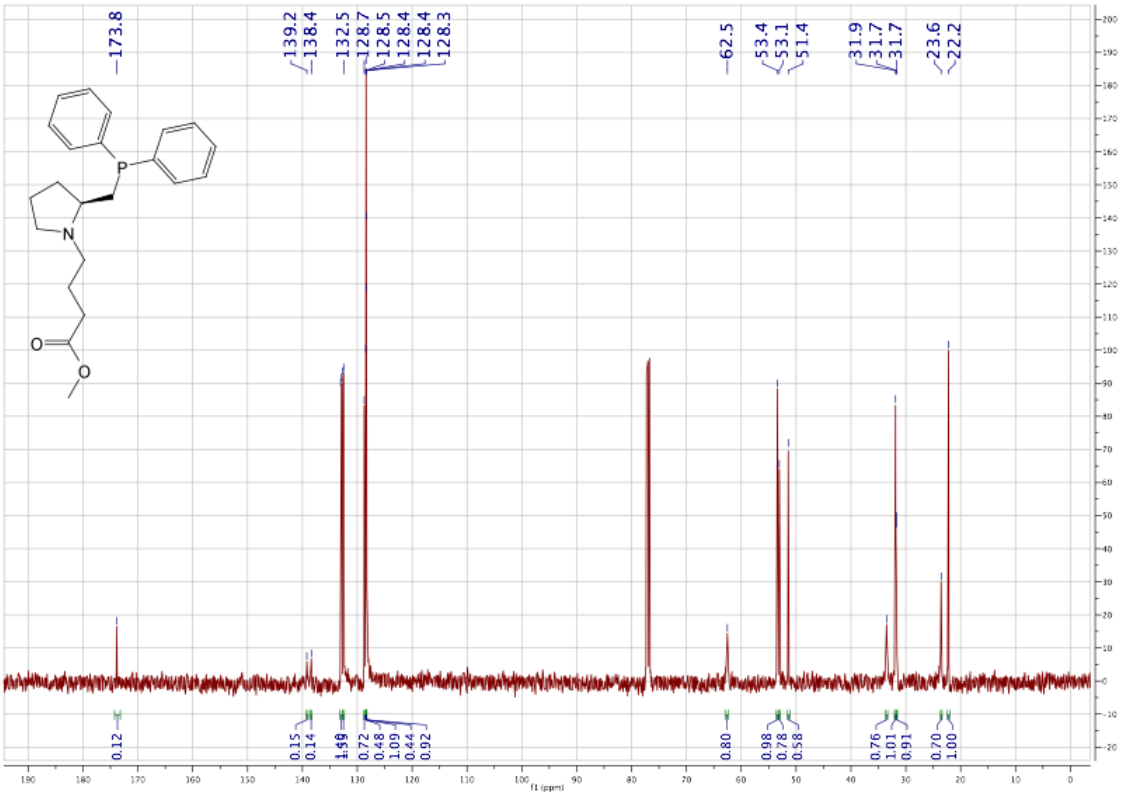
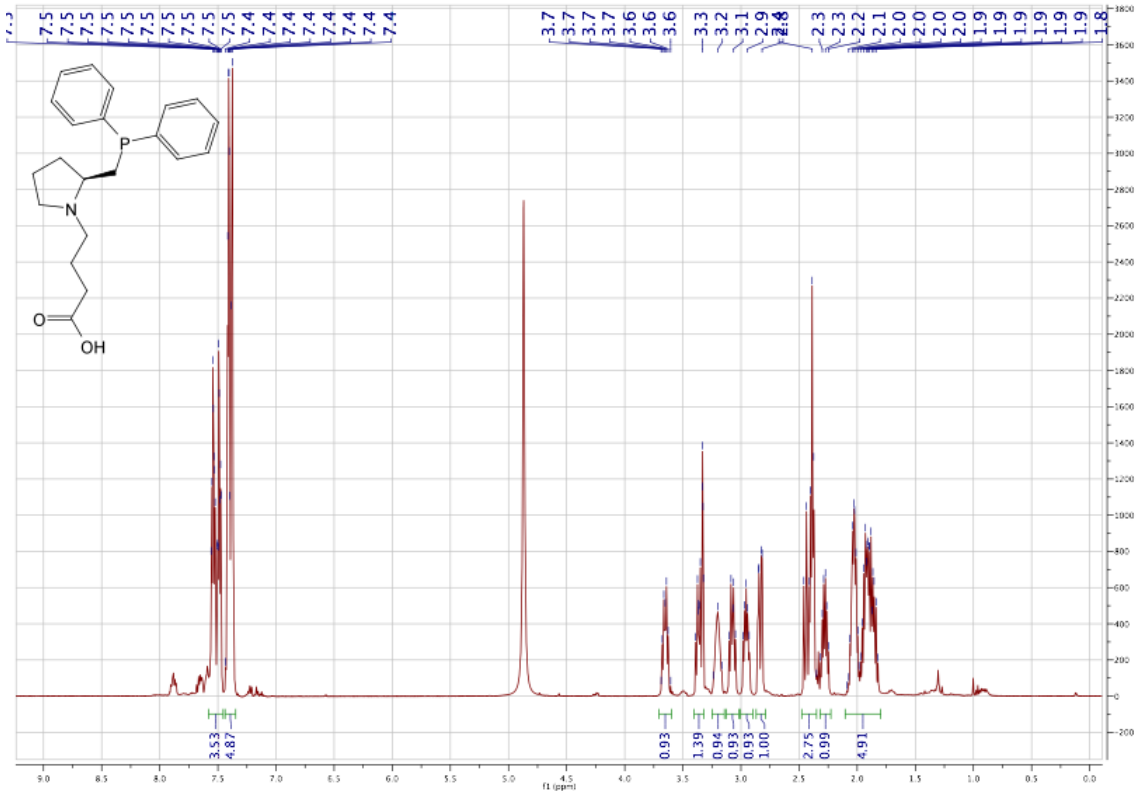
12
10
8
6
4
2
0
-2
Chemical shift /ppm

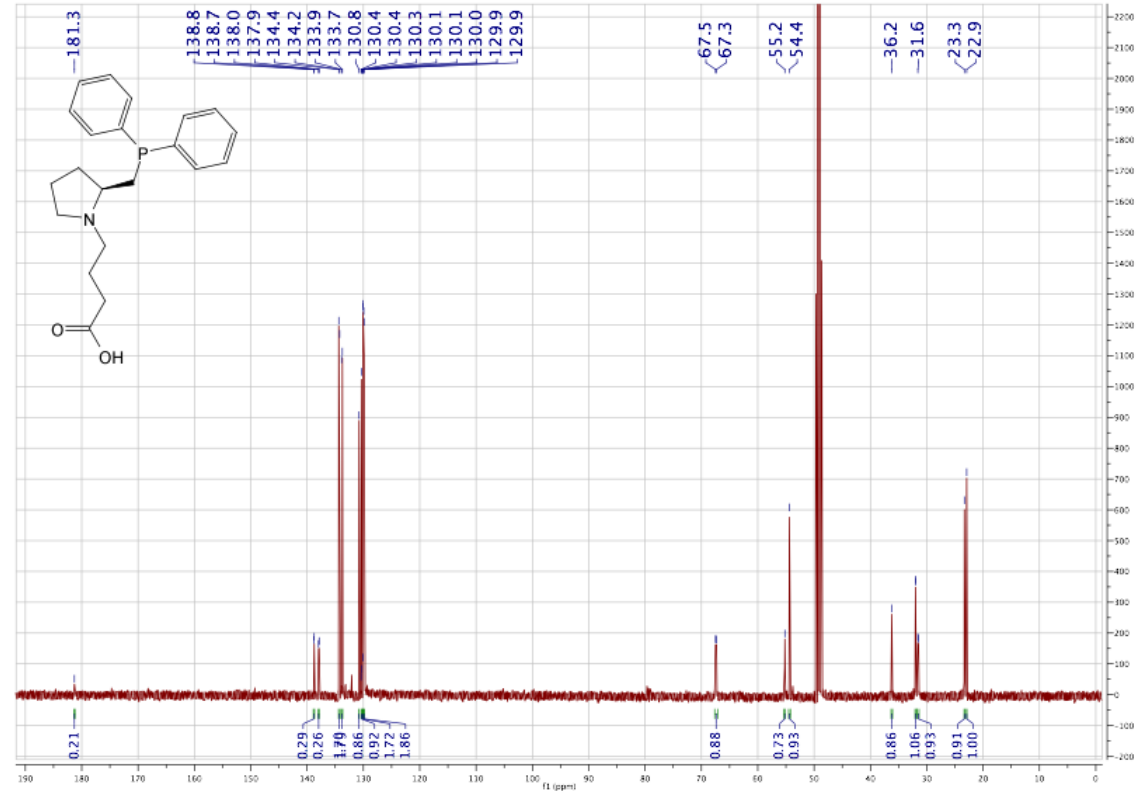
(*S*)-methyl 4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)butanoate (202)



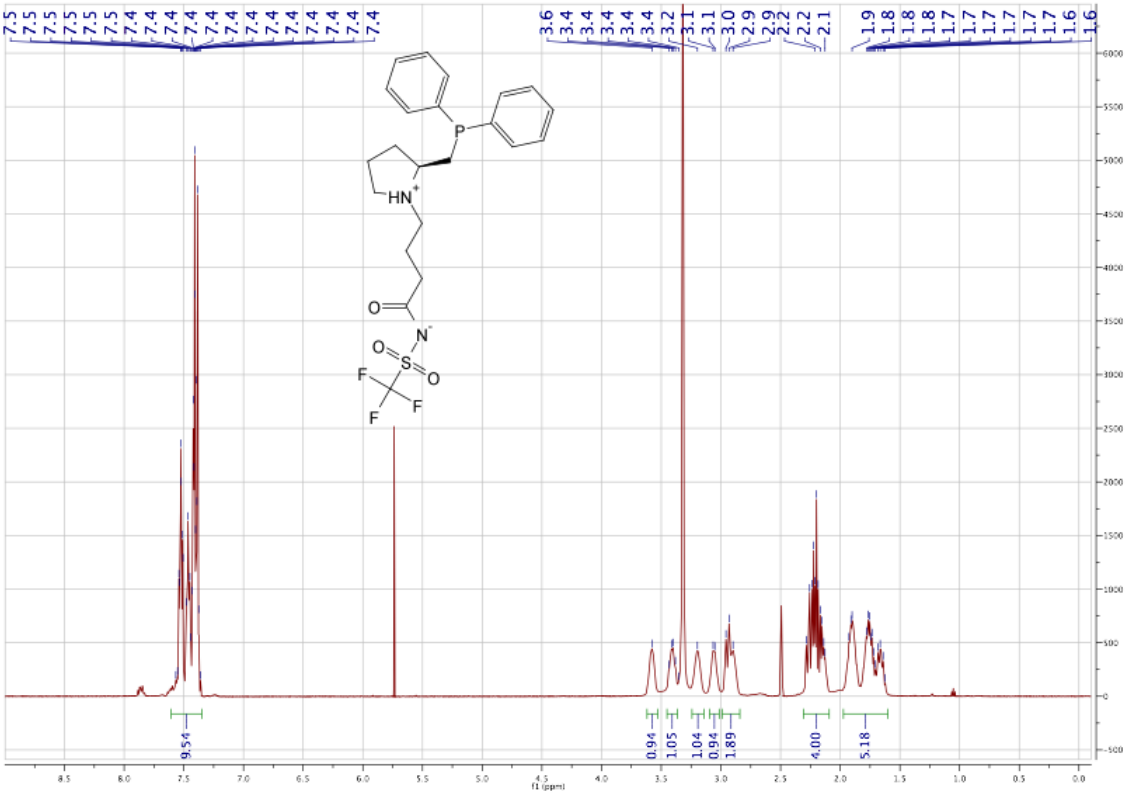


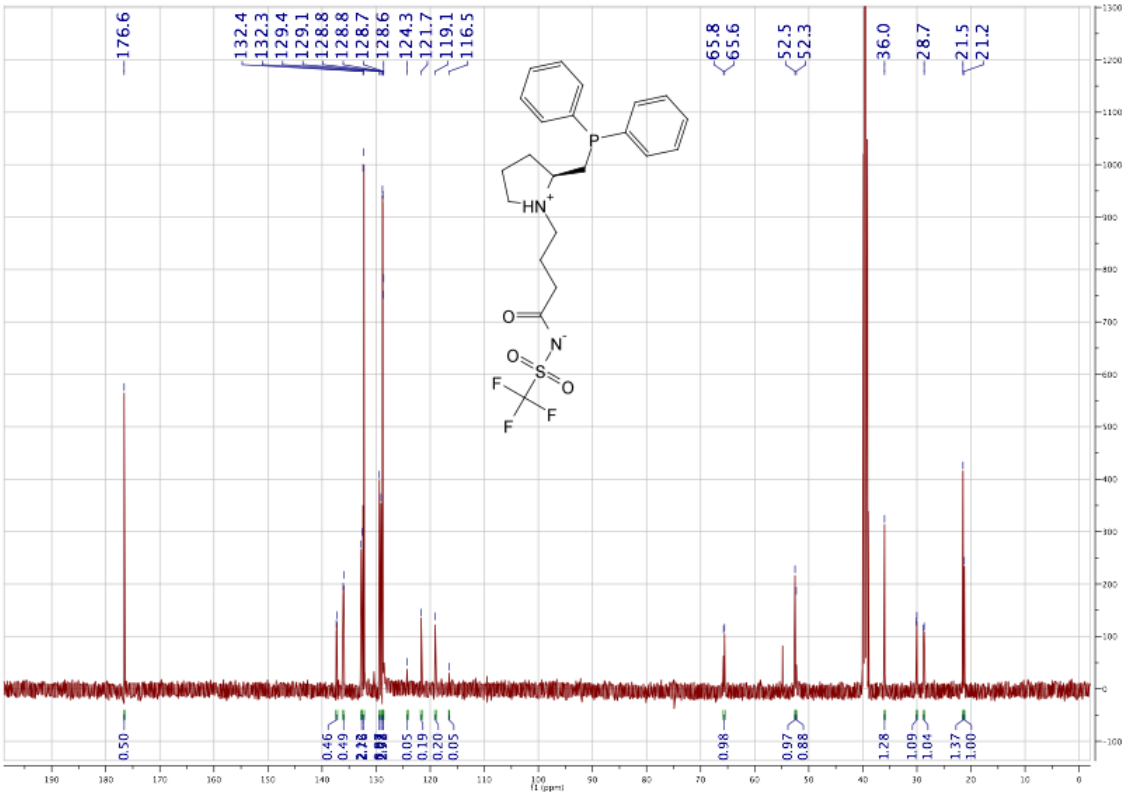
(*S*)-4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)butanoic acid (203)



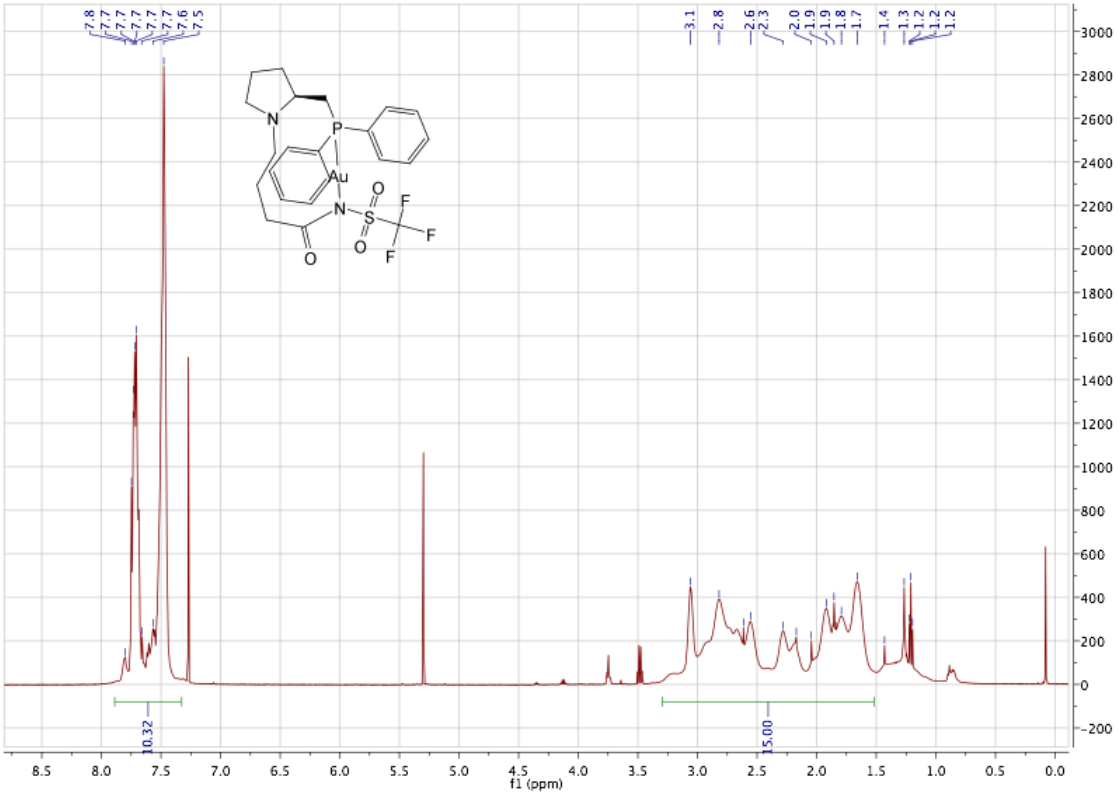


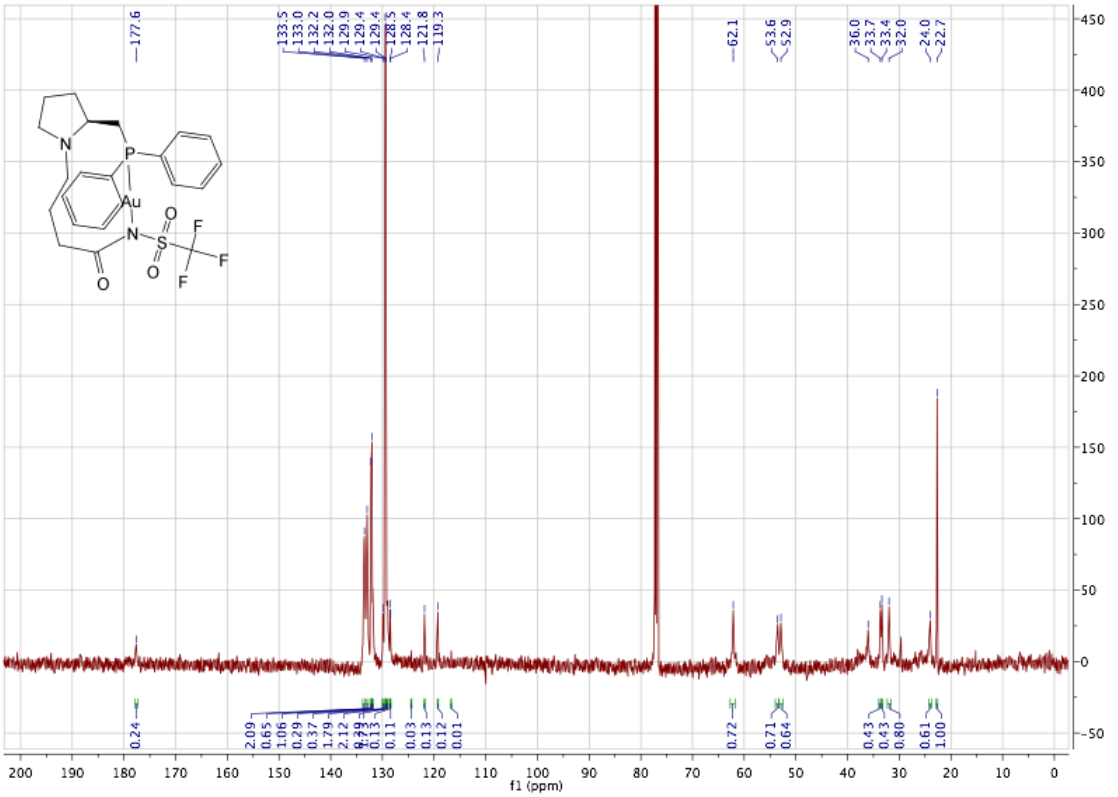
(*S*)-4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-*N*-((trifluoromethyl)sulfonyl)butanamide (205)

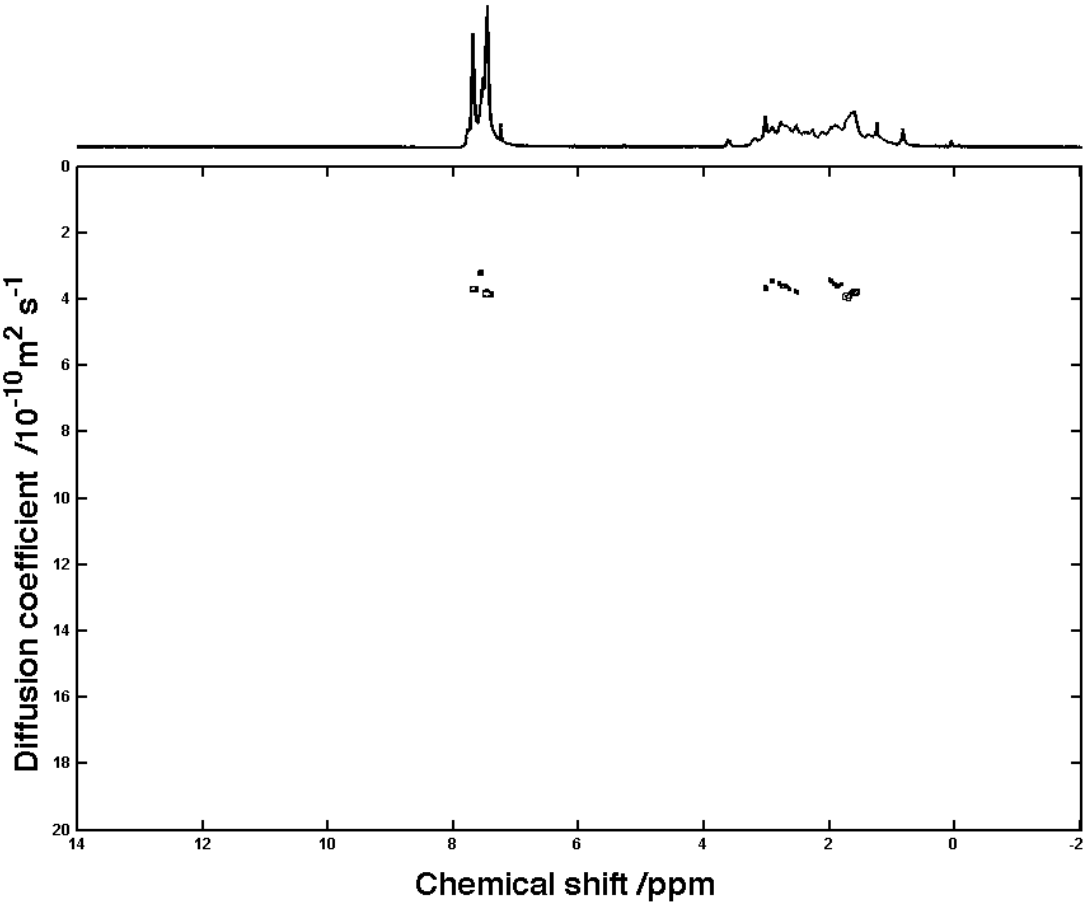




Bidentate Gold(I) complex – monomer and dimer (208/209)






Diffusion coefficient /10-10m2 s-1
0
2
4
6
8
10
12
14
16
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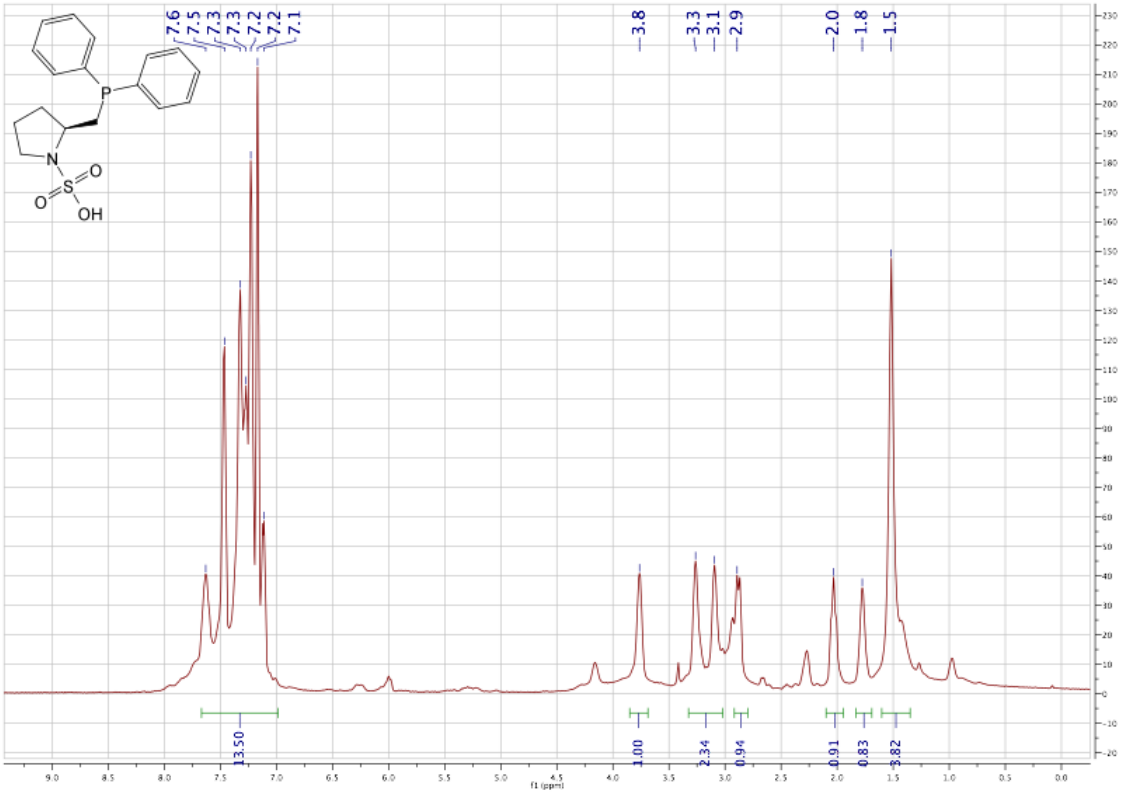
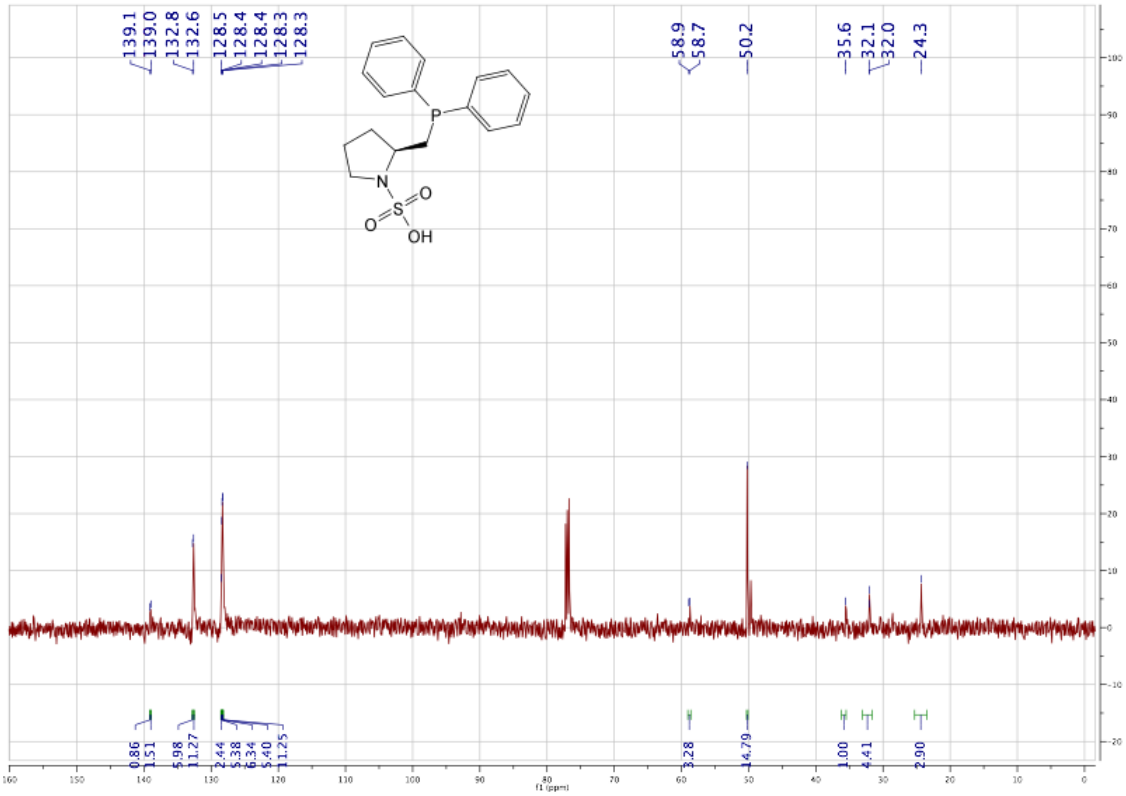
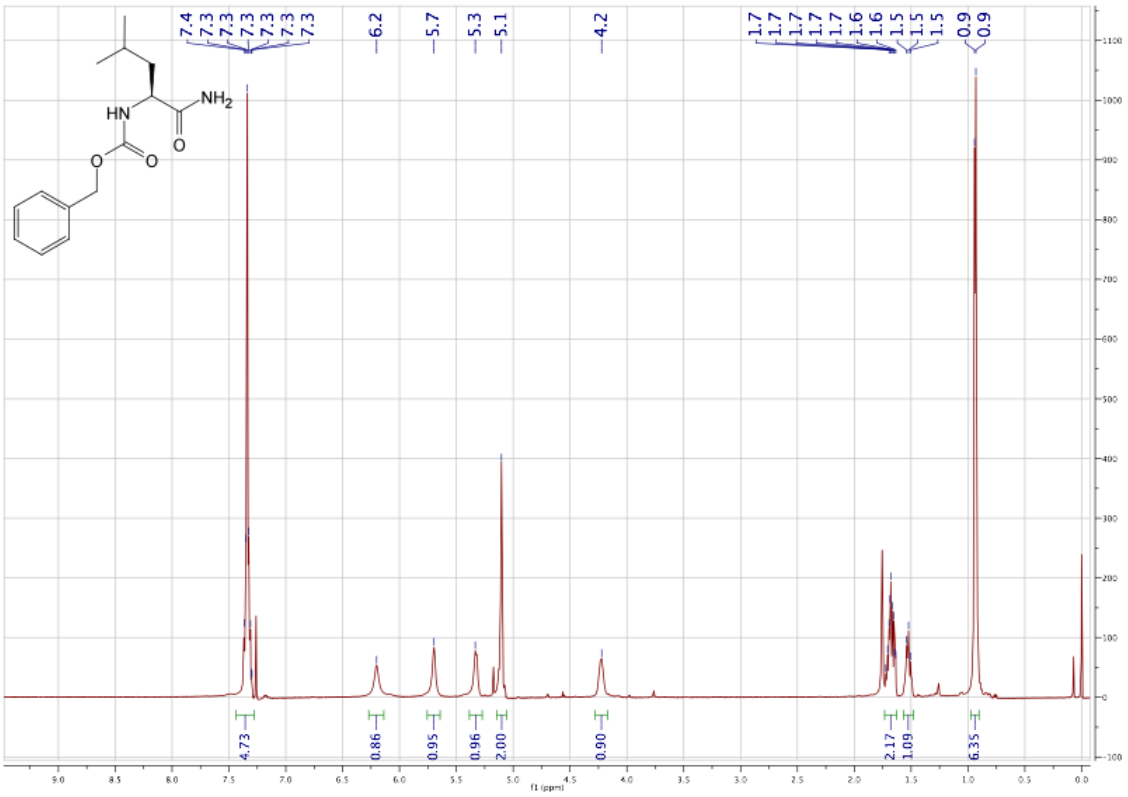
20
14
12
10
8
6
4
2
0
-2
Chemical shift /ppm

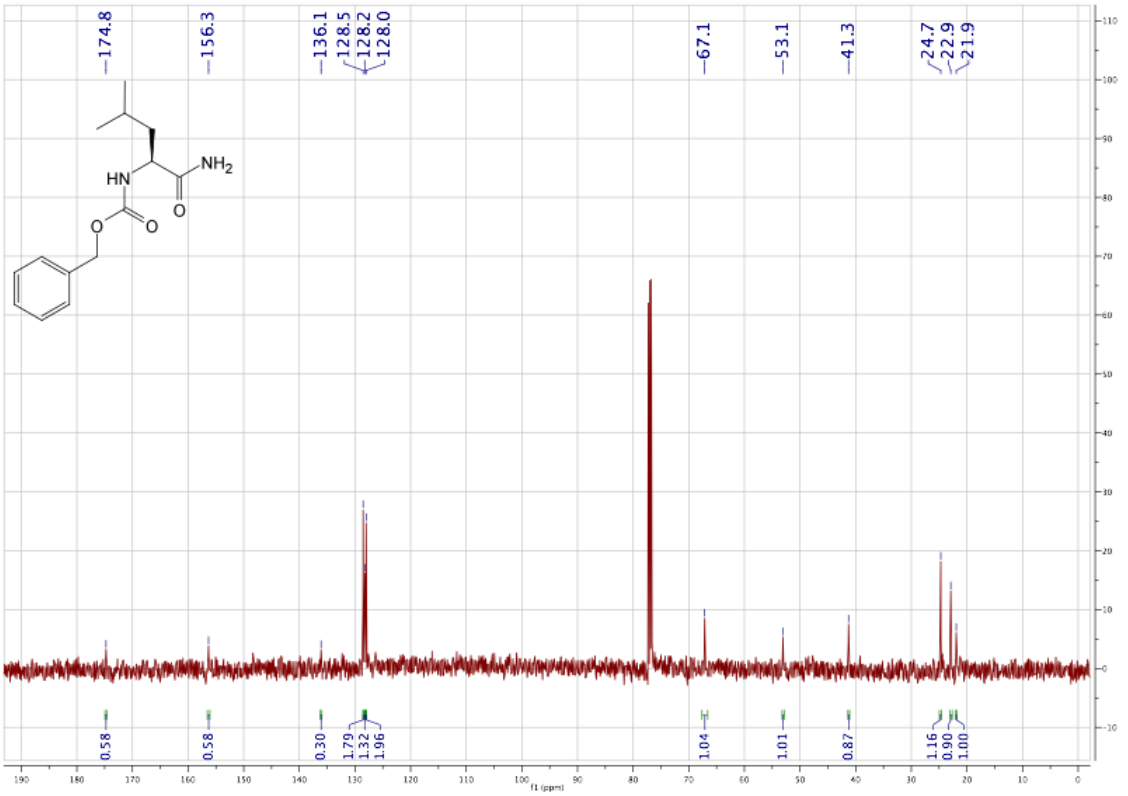
(*S*)-2-((diphenylphosphino)methyl)pyrrolidine-1-sulfonic acid (180)



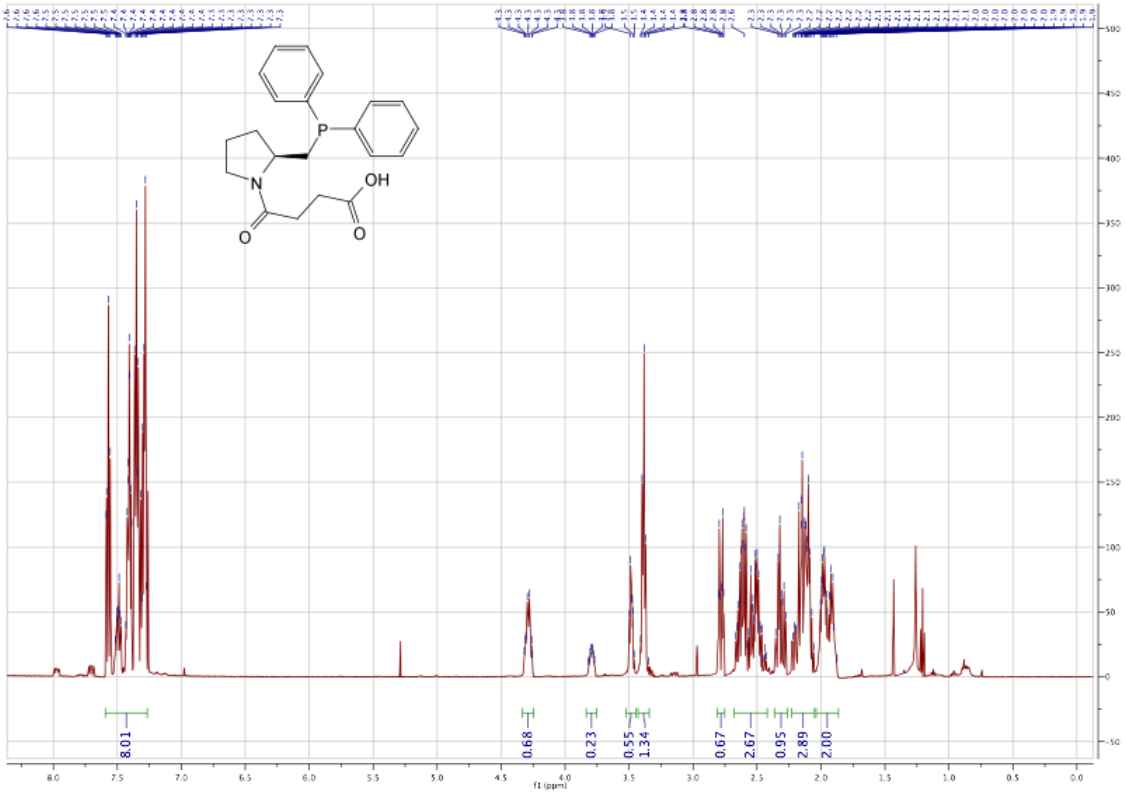


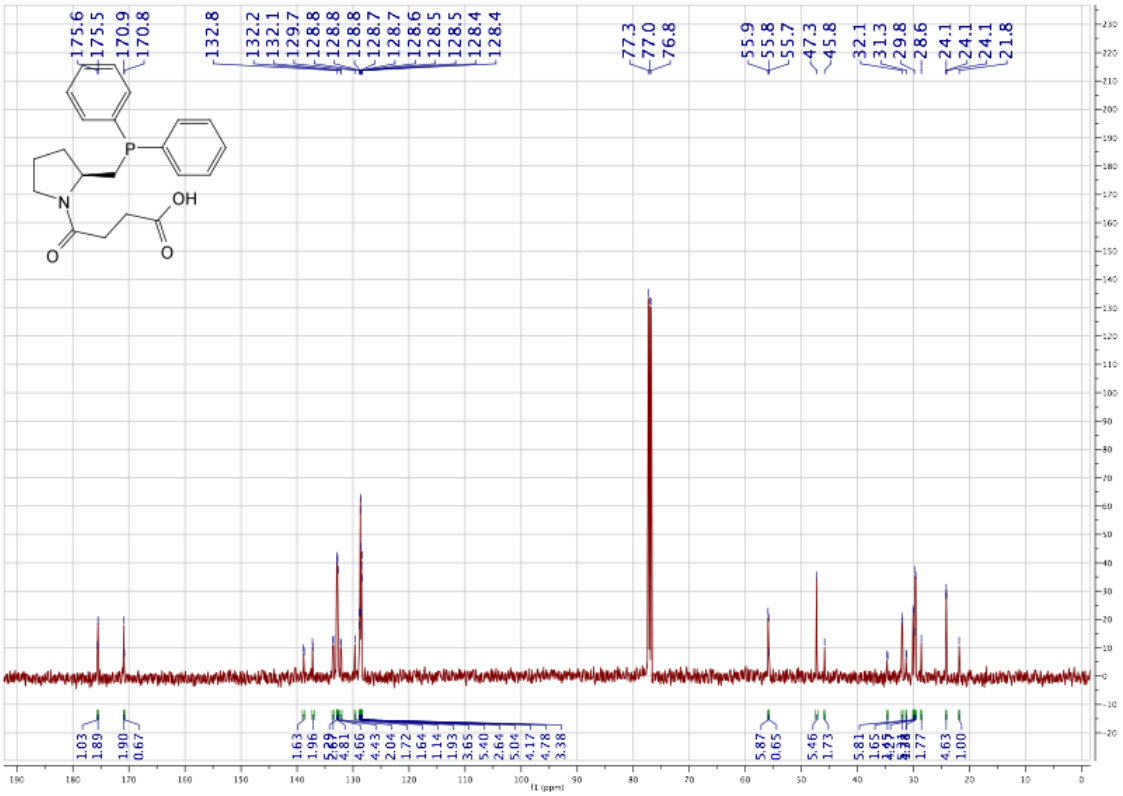
(*S*)-benzyl (1-amino-4-methyl-1-oxopentan-2-yl)carbamate (146)





(*S*)-4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-4-oxobutanoic acid (182)





7. Appendix

Triphenylphosphine gold (*S*)-methyl 2-(trifluoromethylsulfonamido)butanoate (130a)

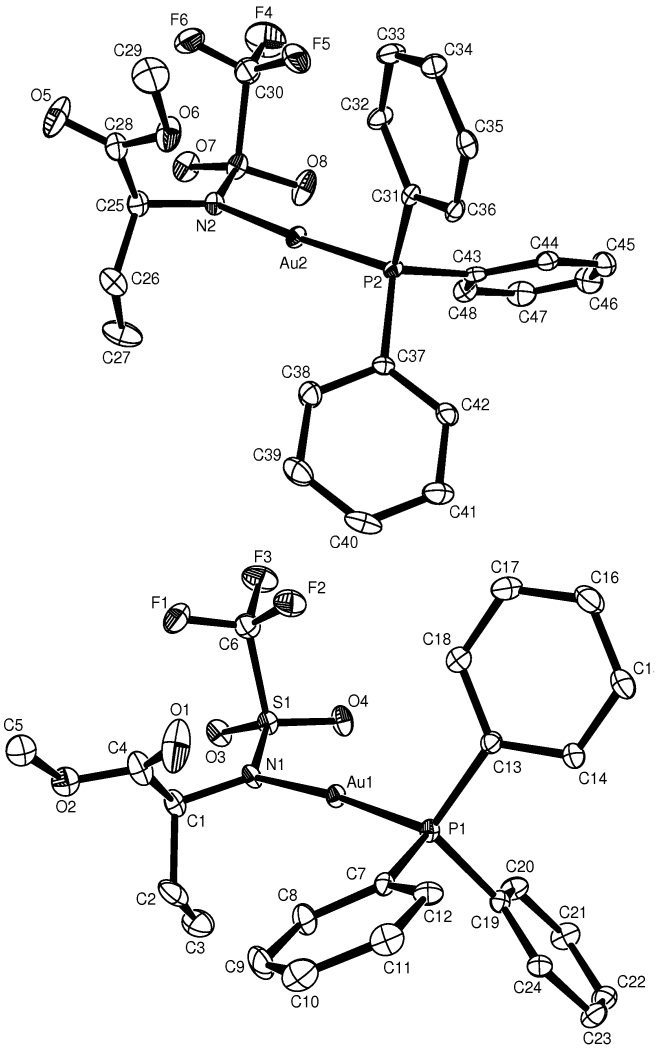


Table 1. Crystal data and structure refinement for Au[N{CH(Et)CO_2Me}Tf](PPh_3).

Identification code	oct1109
Empirical formula	C24 H24 Au F3 N O4 P S
Formula weight	707.44
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* 2_1 (No.4)

Unit cell dimensions	a = 14.3905(2) Å	a= 90°.
	b = 8.5649(1) Å	b= 94.717(1)°.
	c = 21.4697(2) Å	g = 90°.
Volume	2637.25(5) $Å^3$	
Z	4	
Density (calculated)	1.78 Mg/m^3	
Absorption coefficient	5.77 mm^{-1}	
F(000)	1376	
Crystal size	0.20 x 0.14 x 0.10 mm^3	
Theta range for data collection	3.43 to 27.10°.	
Index ranges	-18<=h<=18, -10<=k<=10, -27<=l<=27	
Reflections collected	40715	
Independent reflections	11544 [R(int) = 0.052]	
Completeness to theta = 27.10°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4557 and 0.3919	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11544 / 3 / 633	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.027, wR2 = 0.054	
R indices (all data)	R1 = 0.031, wR2 = 0.055	
Absolute structure parameter	-0.006(4)	
Largest diff. peak and hole	0.56 and -0.78 $e.Å^{-3}$	

There are two independant molecules in the unit cell that differ principally in the orientation of the $-CO_2Me$ groups; the OMe group from compound Au(1) is disordered over two positions and was refined with isotropic carbon and oxygen atoms

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for oct1109. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	7588(1)	4566(1)	7007(1)	21(1)
Au(2)	7479(1)	2396(1)	2060(1)	22(1)
S(1)	7348(1)	4611(2)	8455(1)	24(1)
S(2)	8348(1)	1512(2)	3366(1)	29(1)
P(1)	7640(1)	3614(2)	6043(1)	19(1)
P(2)	7610(1)	3290(2)	1099(1)	19(1)
F(1)	5834(2)	6295(4)	8494(2)	52(1)
F(2)	5664(2)	4264(4)	7901(1)	46(1)
F(3)	5746(2)	4009(5)	8902(2)	57(1)
F(4)	9776(3)	-348(7)	3532(2)	100(2)
F(5)	9154(3)	-316(5)	2591(2)	71(1)
F(6)	8493(3)	-1538(4)	3299(2)	63(1)
O(1)	6622(4)	7661(7)	7103(2)	70(2)
O(3)	7663(3)	5292(5)	9047(1)	33(1)
O(4)	7488(3)	2979(4)	8358(2)	35(1)
O(5)	6100(4)	-2045(5)	3054(2)	67(1)
O(6)	6687(3)	-950(5)	2241(2)	46(1)
O(7)	8217(3)	1344(5)	4018(2)	42(1)
O(8)	8937(3)	2712(5)	3156(2)	49(1)
N(1)	7642(3)	5578(5)	7883(2)	22(1)
N(2)	7416(3)	1487(6)	2936(2)	22(1)
C(1)	7790(3)	7260(6)	7966(2)	28(1)
C(2)	8769(4)	7696(8)	7783(3)	47(2)
C(3)	9531(4)	6960(9)	8219(3)	60(2)

C(4)	7042(4)	8143(7)	7562(2)	38(1)
C(6)	6083(4)	4807(7)	8437(2)	34(1)
C(7)	7721(3)	5207(6)	5490(2)	21(1)
C(8)	8036(4)	6639(7)	5716(2)	31(1)
C(9)	8077(4)	7904(7)	5307(3)	39(1)
C(10)	7843(4)	7721(7)	4682(3)	39(2)
C(11)	7550(4)	6283(7)	4451(2)	32(1)
C(12)	7486(3)	5020(7)	4850(2)	25(1)
C(13)	6633(3)	2475(7)	5751(2)	21(1)
C(14)	6706(4)	1373(7)	5277(2)	31(1)
C(15)	5923(4)	540(8)	5052(3)	44(2)
C(16)	5077(4)	783(8)	5291(3)	39(2)
C(17)	5000(4)	1864(7)	5758(3)	34(1)
C(18)	5772(3)	2718(7)	5987(2)	28(1)
C(19)	8632(3)	2343(7)	5977(2)	20(1)
C(20)	8908(3)	1401(7)	6490(2)	29(1)
C(21)	9654(4)	369(8)	6460(2)	34(1)
C(22)	10122(4)	277(7)	5923(3)	33(1)
C(23)	9843(4)	1209(7)	5410(2)	31(1)
C(24)	9097(3)	2250(7)	5441(2)	25(1)
C(25)	6611(3)	614(6)	3149(2)	29(1)
C(26)	5731(4)	1609(7)	3071(2)	38(1)
C(27)	5797(5)	3056(9)	3476(3)	60(2)
C(28)	6451(4)	-947(7)	2823(2)	34(1)
C(29)	6539(5)	-2410(8)	1899(3)	60(2)
C(30)	8980(4)	-275(9)	3191(3)	50(2)
C(31)	7740(3)	1681(6)	566(2)	20(1)
C(32)	8071(4)	254(7)	816(2)	29(1)
C(33)	8174(4)	-1014(7)	433(2)	32(1)
C(34)	7934(4)	-880(6)	-199(2)	29(1)
C(35)	7616(3)	483(7)	-457(2)	26(1)

C(36)	7514(3)	1792(7)	-78(2)	22(1)
C(37)	6603(3)	4402(7)	794(2)	19(1)
C(38)	5744(3)	4105(7)	1015(2)	31(1)
C(39)	4962(4)	4918(8)	797(3)	40(2)
C(40)	5037(4)	6086(8)	355(3)	41(2)
C(41)	5884(4)	6408(8)	133(2)	36(1)
C(42)	6667(4)	5563(7)	349(2)	28(1)
C(43)	8615(3)	4553(8)	1056(2)	24(1)
C(44)	9084(3)	4715(7)	514(2)	26(1)
C(45)	9858(4)	5670(7)	510(3)	38(1)
C(46)	10174(4)	6463(8)	1040(3)	43(2)
C(47)	9710(4)	6336(8)	1578(3)	42(2)
C(48)	8946(4)	5373(7)	1589(2)	30(1)
O(2)	7082(8)	9601(10)	7720(4)	39(3)[a]
C(5)	6407(10)	10558(15)	7345(6)	42(3)[a]
O(2A)	6745(7)	9459(9)	7872(4)	32(2)[b]
C(5A)	6066(11)	10481(17)	7548(8)	54(4)[b]

a 50.3 %, *b* 49.7 %

Table 3. Bond lengths [Å] and angles [°] for oct1109.

Au(1)-N(1)	2.068(4)
Au(1)-P(1)	2.2307(12)
Au(2)-N(2)	2.044(4)
Au(2)-P(2)	2.2244(12)
S(1)-O(4)	1.430(4)
S(1)-O(3)	1.438(3)
S(1)-N(1)	1.567(4)
S(1)-C(6)	1.826(5)
S(2)-O(8)	1.428(4)
S(2)-O(7)	1.435(4)

S(2)-N(2)	1.564(4)
S(2)-C(30)	1.835(7)
P(1)-C(19)	1.810(5)
P(1)-C(13)	1.815(5)
P(1)-C(7)	1.819(5)
P(2)-C(37)	1.810(5)
P(2)-C(31)	1.811(5)
P(2)-C(43)	1.815(6)
F(1)-C(6)	1.332(6)
F(2)-C(6)	1.338(6)
F(3)-C(6)	1.332(6)
F(4)-C(30)	1.309(7)
F(5)-C(30)	1.333(7)
F(6)-C(30)	1.319(8)
O(1)-C(4)	1.188(7)
O(5)-C(28)	1.195(6)
O(6)-C(28)	1.321(6)
O(6)-C(29)	1.456(7)
N(1)-C(1)	1.465(7)
N(2)-C(25)	1.482(6)
C(1)-C(4)	1.525(8)
C(1)-C(2)	1.540(7)
C(2)-C(3)	1.518(9)
C(4)-O(2)	1.294(9)
C(7)-C(8)	1.383(8)
C(7)-C(12)	1.395(7)
C(8)-C(9)	1.399(8)
C(9)-C(10)	1.367(8)
C(10)-C(11)	1.381(9)
C(11)-C(12)	1.387(7)
C(13)-C(18)	1.391(6)

C(13)-C(14)	1.398(7)
C(14)-C(15)	1.387(8)
C(15)-C(16)	1.374(8)
C(16)-C(17)	1.376(8)
C(17)-C(18)	1.386(8)
C(19)-C(24)	1.380(6)
C(19)-C(20)	1.396(7)
C(20)-C(21)	1.396(8)
C(21)-C(22)	1.384(7)
C(22)-C(23)	1.392(8)
C(23)-C(24)	1.401(7)
C(25)-C(28)	1.518(7)
C(25)-C(26)	1.525(7)
C(26)-C(27)	1.513(8)
C(31)-C(36)	1.398(7)
C(31)-C(32)	1.403(7)
C(32)-C(33)	1.378(8)
C(33)-C(34)	1.376(7)
C(34)-C(35)	1.356(7)
C(35)-C(36)	1.400(7)
C(37)-C(38)	1.385(6)
C(37)-C(42)	1.387(7)
C(38)-C(39)	1.373(8)
C(39)-C(40)	1.389(9)
C(40)-C(41)	1.373(8)
C(41)-C(42)	1.387(7)
C(43)-C(48)	1.392(7)
C(43)-C(44)	1.399(6)
C(44)-C(45)	1.382(8)
C(45)-C(46)	1.369(8)
C(46)-C(47)	1.385(8)

C(47)-C(48)	1.376(8)
O(2)-C(5)	1.461(11)

N(1)-Au(1)-P(1)	174.79(12)
N(2)-Au(2)-P(2)	176.79(13)
O(4)-S(1)-O(3)	119.2(2)
O(4)-S(1)-N(1)	110.6(2)
O(3)-S(1)-N(1)	113.1(2)
O(4)-S(1)-C(6)	103.8(2)
O(3)-S(1)-C(6)	102.9(2)
N(1)-S(1)-C(6)	105.5(2)
O(8)-S(2)-O(7)	120.6(2)
O(8)-S(2)-N(2)	109.0(2)
O(7)-S(2)-N(2)	113.5(2)
O(8)-S(2)-C(30)	102.7(3)
O(7)-S(2)-C(30)	102.9(3)
N(2)-S(2)-C(30)	106.4(3)
C(19)-P(1)-C(13)	105.2(3)
C(19)-P(1)-C(7)	107.9(2)
C(13)-P(1)-C(7)	105.7(2)
C(19)-P(1)-Au(1)	112.24(15)
C(13)-P(1)-Au(1)	115.48(14)
C(7)-P(1)-Au(1)	109.87(17)
C(37)-P(2)-C(31)	107.0(2)
C(37)-P(2)-C(43)	106.6(2)
C(31)-P(2)-C(43)	107.3(2)
C(37)-P(2)-Au(2)	112.97(14)
C(31)-P(2)-Au(2)	110.22(16)
C(43)-P(2)-Au(2)	112.36(15)
C(4)-O(2)-C(5)	112.6(8)
C(28)-O(6)-C(29)	116.1(5)

C(1)-N(1)-S(1)	118.1(3)
C(1)-N(1)-Au(1)	121.1(3)
S(1)-N(1)-Au(1)	120.0(2)
C(25)-N(2)-S(2)	118.6(3)
C(25)-N(2)-Au(2)	124.8(3)
S(2)-N(2)-Au(2)	115.9(2)
N(1)-C(1)-C(4)	109.3(4)
N(1)-C(1)-C(2)	109.5(4)
C(4)-C(1)-C(2)	110.7(4)
C(3)-C(2)-C(1)	111.8(5)
O(1)-C(4)-O(2)	124.1(6)
O(1)-C(4)-C(1)	125.9(5)
O(2)-C(4)-C(1)	108.4(5)
F(1)-C(6)-F(3)	107.8(4)
F(1)-C(6)-F(2)	107.8(4)
F(3)-C(6)-F(2)	107.4(4)
F(1)-C(6)-S(1)	111.2(4)
F(3)-C(6)-S(1)	111.1(4)
F(2)-C(6)-S(1)	111.3(3)
C(8)-C(7)-C(12)	119.6(5)
C(8)-C(7)-P(1)	118.2(4)
C(12)-C(7)-P(1)	122.2(4)
C(7)-C(8)-C(9)	119.7(5)
C(10)-C(9)-C(8)	120.5(6)
C(9)-C(10)-C(11)	119.9(5)
C(10)-C(11)-C(12)	120.5(5)
C(11)-C(12)-C(7)	119.7(5)
C(18)-C(13)-C(14)	119.3(5)
C(18)-C(13)-P(1)	120.2(4)
C(14)-C(13)-P(1)	120.5(3)
C(15)-C(14)-C(13)	119.5(5)

C(16)-C(15)-C(14)	120.7(5)
C(15)-C(16)-C(17)	120.1(5)
C(16)-C(17)-C(18)	120.2(5)
C(17)-C(18)-C(13)	120.2(5)
C(24)-C(19)-C(20)	119.9(5)
C(24)-C(19)-P(1)	122.6(4)
C(20)-C(19)-P(1)	117.5(3)
C(19)-C(20)-C(21)	120.0(4)
C(22)-C(21)-C(20)	120.2(5)
C(21)-C(22)-C(23)	119.9(5)
C(22)-C(23)-C(24)	120.0(4)
C(19)-C(24)-C(23)	120.2(5)
N(2)-C(25)-C(28)	113.3(4)
N(2)-C(25)-C(26)	110.4(4)
C(28)-C(25)-C(26)	110.4(4)
C(27)-C(26)-C(25)	112.5(4)
O(5)-C(28)-O(6)	122.8(5)
O(5)-C(28)-C(25)	123.7(5)
O(6)-C(28)-C(25)	113.4(4)
F(4)-C(30)-F(6)	108.4(5)
F(4)-C(30)-F(5)	108.2(5)
F(6)-C(30)-F(5)	107.0(6)
F(4)-C(30)-S(2)	110.6(6)
F(6)-C(30)-S(2)	111.6(4)
F(5)-C(30)-S(2)	110.8(4)
C(36)-C(31)-C(32)	118.8(5)
C(36)-C(31)-P(2)	123.1(4)
C(32)-C(31)-P(2)	118.1(4)
C(33)-C(32)-C(31)	120.5(5)
C(34)-C(33)-C(32)	119.4(5)
C(35)-C(34)-C(33)	121.6(5)

C(34)-C(35)-C(36)	120.0(4)
C(31)-C(36)-C(35)	119.6(5)
C(38)-C(37)-C(42)	118.7(5)
C(38)-C(37)-P(2)	119.3(4)
C(42)-C(37)-P(2)	122.0(3)
C(39)-C(38)-C(37)	121.3(5)
C(38)-C(39)-C(40)	119.4(5)
C(41)-C(40)-C(39)	120.2(5)
C(40)-C(41)-C(42)	120.0(6)
C(37)-C(42)-C(41)	120.4(5)
C(48)-C(43)-C(44)	118.5(5)
C(48)-C(43)-P(2)	118.7(4)
C(44)-C(43)-P(2)	122.8(4)
C(45)-C(44)-C(43)	120.5(5)
C(46)-C(45)-C(44)	120.0(5)
C(45)-C(46)-C(47)	120.3(6)
C(48)-C(47)-C(46)	120.1(6)
C(47)-C(48)-C(43)	120.6(5)

Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-leucinate (130b)

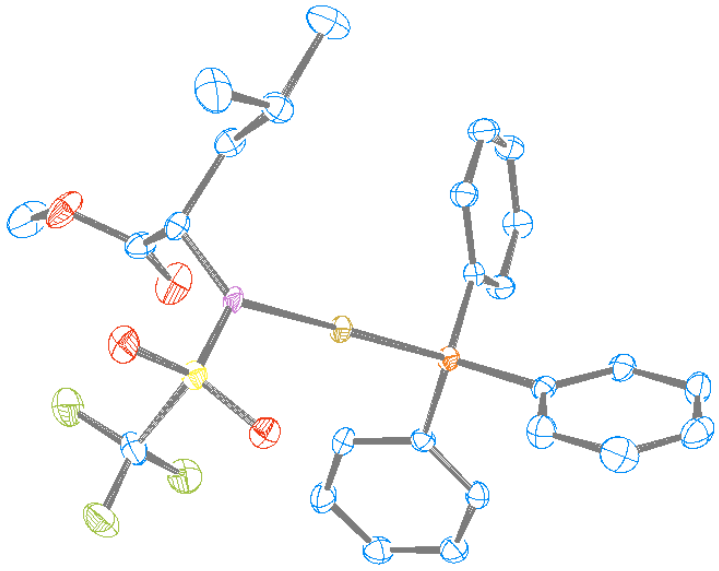


Table 1. Crystal data and structure refinement for import.

Identification code	shelxl
Empirical formula	C26 H28 Au F3 N O4 P S
Formula weight	735.49
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21
Unit cell dimensions	a = 8.8582(2) A alpha = 90 deg.
	b = 15.4083(3) A beta = 109.3330(10) deg.
	c = 11.0582(2) A gamma = 90 deg.
Volume	1424.22(5) A^3
Z, Calculated density	2, 1.715 Mg/m^3
Absorption coefficient	5.345 mm^-1
F(000)	720
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	3.59 to 27.07 deg.
Limiting indices	-11<=h<=11, -16<=k<=19, -14<=l<=14

Reflections collected / unique	17219 / 5926 [R(int) = 0.0424]
Completeness to theta = 27.07	99.4 %
Max. and min. transmission	0.4145 and 0.2970
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5926 / 1 / 335
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0738
R indices (all data)	R1 = 0.0317, wR2 = 0.0747
Absolute structure parameter	0.080(6)
Largest diff. peak and hole	1.617 and -3.156 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for import.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2028(7)	3571(4)	5447(6)	28(1)
C(2)	2986(6)	3530(3)	6702(4)	33(1)
C(3)	3825(7)	4259(4)	7296(5)	42(1)
C(4)	3702(8)	5030(4)	6622(6)	43(1)
C(5)	2748(8)	5075(4)	5360(6)	45(1)
C(6)	1902(7)	4352(4)	4754(5)	36(1)
C(7)	-1099(5)	2801(3)	4780(4)	26(1)
C(8)	-1286(6)	3260(3)	5807(5)	33(1)
C(9)	-2799(6)	3354(4)	5912(5)	38(1)
C(10)	-4122(6)	3001(4)	4994(6)	42(1)
C(11)	-3943(6)	2538(5)	3961(5)	41(1)
C(12)	-2436(6)	2460(3)	3853(5)	34(1)
C(13)	1673(7)	1675(4)	5432(5)	26(1)
C(14)	1176(6)	1351(4)	6420(5)	33(1)

C(15)	1804(7)	569(4)	7012(5)	43(1)
C(16)	2933(8)	126(4)	6637(6)	46(2)
C(17)	3433(8)	443(4)	5696(7)	50(2)
C(18)	2811(7)	1214(4)	5085(6)	38(1)
C(19)	3105(7)	3630(3)	614(5)	38(1)
C(20)	-890(6)	2996(3)	-356(4)	28(1)
C(21)	-1030(6)	3956(3)	-115(5)	35(1)
C(22)	-1995(10)	5285(4)	-1132(8)	67(2)
C(23)	-2403(5)	2549(4)	-301(4)	34(1)
C(24)	-2502(7)	1572(3)	-514(6)	38(1)
C(25)	-4103(8)	1238(5)	-416(8)	56(2)
C(26)	-2304(11)	1311(5)	-1773(7)	60(2)
Au(1)	692(1)	2637(1)	2542(1)	26(1)
F(1)	3329(4)	3918(2)	1802(3)	47(1)
F(2)	2214(5)	4215(2)	-196(4)	55(1)
F(3)	4529(4)	3612(2)	455(4)	55(1)
N(1)	551(4)	2638(6)	629(3)	25(1)
O(1)	1898(5)	2422(2)	-998(3)	40(1)
O(2)	3268(4)	2031(2)	1271(3)	34(1)
O(3)	-644(6)	4310(3)	908(4)	55(1)
O(4)	-1698(6)	4365(3)	-1228(4)	54(1)
P(1)	837(1)	2661(2)	4593(1)	24(1)
S(1)	2146(1)	2558(1)	330(1)	26(1)

Table 3. Bond lengths [A] and angles [deg] for import.

C(1)-C(2)	1.367(7)
C(1)-C(6)	1.410(8)
C(1)-P(1)	1.821(6)
C(2)-C(3)	1.387(8)
C(2)-H(2)	0.9500

C(3)-C(4)	1.387(9)
C(3)-H(3)	0.9500
C(4)-C(5)	1.373(9)
C(4)-H(4)	0.9500
C(5)-C(6)	1.386(8)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(12)	1.388(7)
C(7)-C(8)	1.393(6)
C(7)-P(1)	1.807(5)
C(8)-C(9)	1.390(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.383(8)
C(9)-H(9)	0.9500
C(10)-C(11)	1.399(8)
C(10)-H(10)	0.9500
C(11)-C(12)	1.384(6)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(18)	1.387(8)
C(13)-C(14)	1.399(8)
C(13)-P(1)	1.806(6)
C(14)-C(15)	1.396(8)
C(14)-H(14)	0.9500
C(15)-C(16)	1.383(9)
C(15)-H(15)	0.9500
C(16)-C(17)	1.350(9)
C(16)-H(16)	0.9500
C(17)-C(18)	1.388(9)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500

C(19)-F(3)	1.330(6)
C(19)-F(2)	1.330(6)
C(19)-F(1)	1.338(6)
C(19)-S(1)	1.836(5)
C(20)-N(1)	1.483(6)
C(20)-C(21)	1.515(7)
C(20)-C(23)	1.526(7)
C(20)-H(20)	1.0000
C(21)-O(3)	1.200(7)
C(21)-O(4)	1.334(7)
C(22)-O(4)	1.452(8)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-C(24)	1.521(8)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(26)	1.515(9)
C(24)-C(25)	1.545(8)
C(24)-H(24)	1.0000
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
Au(1)-N(1)	2.077(3)
Au(1)-P(1)	2.2283(9)
N(1)-S(1)	1.560(3)
O(1)-S(1)	1.427(3)
O(2)-S(1)	1.430(4)

C(2)-C(1)-C(6)	120.1(5)
C(2)-C(1)-P(1)	123.3(4)
C(6)-C(1)-P(1)	116.5(4)
C(1)-C(2)-C(3)	119.9(5)
C(1)-C(2)-H(2)	120.1
C(3)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	120.3(5)
C(2)-C(3)-H(3)	119.8
C(4)-C(3)-H(3)	119.8
C(5)-C(4)-C(3)	120.1(6)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	120.2(5)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(5)-C(6)-C(1)	119.3(5)
C(5)-C(6)-H(6)	120.3
C(1)-C(6)-H(6)	120.3
C(12)-C(7)-C(8)	119.4(4)
C(12)-C(7)-P(1)	118.7(4)
C(8)-C(7)-P(1)	121.9(4)
C(9)-C(8)-C(7)	119.9(5)
C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0
C(10)-C(9)-C(8)	120.3(5)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	120.1(5)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9

C(12)-C(11)-C(10)	119.2(5)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(11)-C(12)-C(7)	121.0(5)
C(11)-C(12)-H(12)	119.5
C(7)-C(12)-H(12)	119.5
C(18)-C(13)-C(14)	118.6(5)
C(18)-C(13)-P(1)	120.0(4)
C(14)-C(13)-P(1)	121.4(4)
C(13)-C(14)-C(15)	119.6(5)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
C(16)-C(15)-C(14)	120.1(5)
C(16)-C(15)-H(15)	120.0
C(14)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.5(5)
C(17)-C(16)-H(16)	119.8
C(15)-C(16)-H(16)	119.8
C(16)-C(17)-C(18)	120.4(6)
C(16)-C(17)-H(17)	119.8
C(18)-C(17)-H(17)	119.8
C(17)-C(18)-C(13)	120.8(6)
C(17)-C(18)-H(18)	119.6
C(13)-C(18)-H(18)	119.6
F(3)-C(19)-F(2)	107.6(4)
F(3)-C(19)-F(1)	107.3(5)
F(2)-C(19)-F(1)	107.4(4)
F(3)-C(19)-S(1)	111.3(4)
F(2)-C(19)-S(1)	110.9(4)
F(1)-C(19)-S(1)	112.1(3)
N(1)-C(20)-C(21)	109.6(5)

N(1)-C(20)-C(23)	110.9(4)
C(21)-C(20)-C(23)	108.0(4)
N(1)-C(20)-H(20)	109.5
C(21)-C(20)-H(20)	109.5
C(23)-C(20)-H(20)	109.5
O(3)-C(21)-O(4)	123.8(5)
O(3)-C(21)-C(20)	126.5(5)
O(4)-C(21)-C(20)	109.6(4)
O(4)-C(22)-H(22A)	109.5
O(4)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
O(4)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(24)-C(23)-C(20)	116.6(4)
C(24)-C(23)-H(23A)	108.2
C(20)-C(23)-H(23A)	108.2
C(24)-C(23)-H(23B)	108.2
C(20)-C(23)-H(23B)	108.2
H(23A)-C(23)-H(23B)	107.3
C(26)-C(24)-C(23)	112.7(5)
C(26)-C(24)-C(25)	111.3(6)
C(23)-C(24)-C(25)	109.1(5)
C(26)-C(24)-H(24)	107.8
C(23)-C(24)-H(24)	107.8
C(25)-C(24)-H(24)	107.8
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5

H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
N(1)-Au(1)-P(1)	179.0(3)
C(20)-N(1)-S(1)	119.5(3)
C(20)-N(1)-Au(1)	119.7(3)
S(1)-N(1)-Au(1)	117.56(17)
C(21)-O(4)-C(22)	115.4(5)
C(13)-P(1)-C(7)	106.6(3)
C(13)-P(1)-C(1)	108.2(2)
C(7)-P(1)-C(1)	104.9(3)
C(13)-P(1)-Au(1)	112.6(2)
C(7)-P(1)-Au(1)	112.41(15)
C(1)-P(1)-Au(1)	111.7(2)
O(1)-S(1)-O(2)	119.9(2)
O(1)-S(1)-N(1)	112.8(2)
O(2)-S(1)-N(1)	110.5(3)
O(1)-S(1)-C(19)	102.3(2)
O(2)-S(1)-C(19)	102.5(2)
N(1)-S(1)-C(19)	107.0(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for import.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	24(2)	32(3)	29(3)	0(2)	11(2)	0(2)
C(2)	36(2)	40(3)	26(2)	2(2)	14(2)	-5(2)
C(3)	39(3)	53(3)	30(3)	-3(2)	7(2)	-11(3)
C(4)	42(3)	42(3)	43(4)	-6(2)	10(3)	-8(3)
C(5)	52(4)	35(3)	42(3)	10(2)	6(3)	-2(3)
C(6)	38(3)	38(3)	28(2)	9(2)	6(2)	2(2)
C(7)	28(2)	25(4)	25(2)	3(2)	11(2)	0(2)
C(8)	28(2)	46(3)	27(2)	-6(2)	12(2)	-2(2)
C(9)	39(3)	48(3)	34(3)	-9(2)	21(2)	3(2)
C(10)	26(2)	54(3)	46(3)	6(2)	13(2)	0(2)
C(11)	30(2)	45(4)	41(2)	-2(3)	5(2)	-3(3)
C(12)	32(2)	44(4)	27(2)	-3(2)	10(2)	-4(2)
C(13)	26(3)	31(3)	20(2)	-1(2)	4(2)	-2(2)
C(14)	35(2)	41(3)	22(2)	-1(2)	8(2)	-1(2)
C(15)	49(3)	44(3)	32(3)	9(2)	9(2)	-4(2)
C(16)	46(3)	31(3)	48(3)	1(2)	-2(3)	4(2)
C(17)	47(4)	34(3)	70(5)	-6(3)	22(3)	7(3)
C(18)	43(3)	40(3)	37(3)	1(2)	20(2)	5(2)
C(19)	47(3)	34(3)	38(3)	1(2)	20(2)	-9(2)
C(20)	34(2)	28(2)	21(2)	-1(2)	7(2)	4(2)
C(21)	34(3)	31(2)	37(3)	-4(2)	5(2)	0(2)
C(22)	74(5)	26(3)	74(5)	6(3)	-10(4)	3(3)
C(23)	32(2)	32(3)	34(2)	-2(3)	7(2)	6(2)
C(24)	36(3)	32(2)	46(3)	-2(2)	15(2)	-2(2)
C(25)	39(3)	45(3)	87(5)	-6(3)	25(3)	-5(3)
C(26)	93(5)	40(3)	50(4)	-14(3)	28(4)	-20(3)
Au(1)	31(1)	34(1)	16(1)	-1(1)	11(1)	-1(1)
F(1)	59(2)	39(2)	42(2)	-12(1)	14(2)	-14(2)

F(2)	63(2)	38(2)	64(2)	15(2)	21(2)	-3(2)
F(3)	45(2)	64(2)	64(2)	3(2)	30(2)	-12(2)
N(1)	29(2)	33(2)	13(1)	2(3)	8(1)	1(4)
O(1)	53(2)	50(3)	22(1)	-10(1)	21(1)	-2(2)
O(2)	34(2)	35(2)	33(2)	-1(2)	12(2)	7(1)
O(3)	80(3)	42(2)	41(2)	-12(2)	18(2)	13(2)
O(4)	70(3)	28(2)	41(2)	1(2)	-11(2)	9(2)
P(1)	26(1)	32(1)	15(1)	0(1)	10(1)	0(1)
S(1)	32(1)	29(1)	20(1)	-4(1)	12(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for import.

	x	y	z	U(eq)
H(2)	3077	3003	7166	40
H(3)	4487	4231	8169	50
H(4)	4279	5528	7034	52
H(5)	2667	5604	4901	54
H(6)	1244	4381	3880	43
H(8)	-381	3508	6435	39
H(9)	-2924	3661	6617	45
H(10)	-5155	3073	5064	50
H(11)	-4844	2281	3342	49
H(12)	-2315	2169	3133	41
H(14)	415	1661	6688	40
H(15)	1456	341	7673	51
H(16)	3359	-405	7044	55
H(17)	4215	136	5450	60
H(18)	3170	1430	4422	46
H(20)	-796	2912	-1225	33

H(22A)	-2476	5528	-1994	100
H(22B)	-983	5582	-695	100
H(22C)	-2727	5365	-643	100
H(23A)	-2506	2669	548	40
H(23B)	-3334	2819	-954	40
H(24)	-1615	1299	193	45
H(25A)	-4201	1420	403	84
H(25B)	-4128	603	-468	84
H(25C)	-4993	1478	-1122	84
H(26A)	-2366	678	-1858	90
H(26B)	-1261	1510	-1792	90
H(26C)	-3156	1576	-2483	90

Table 6. Torsion angles [deg] for import.

Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*L*)-valinate (130c)

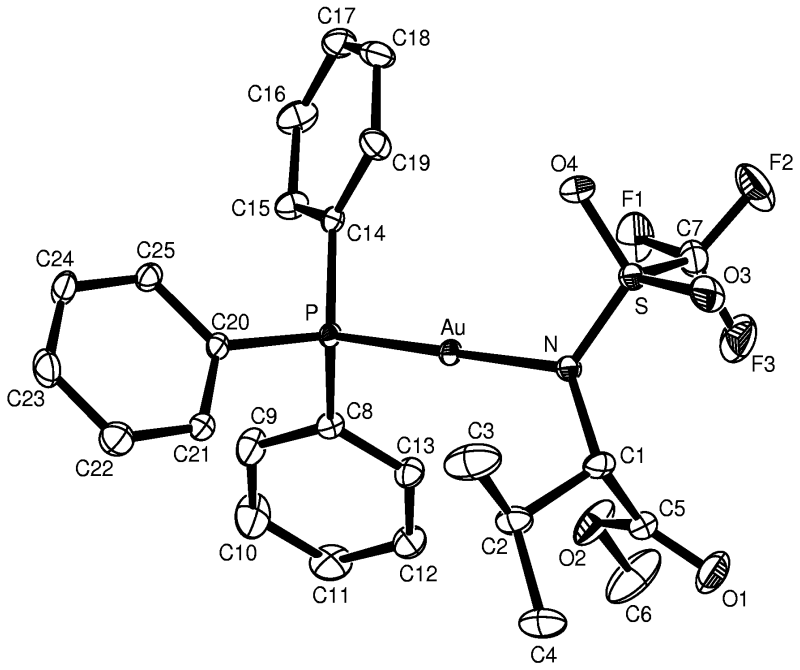


Table 1. Crystal data and structure refinement for Au(NTf{CH(^{i}Pr)CO_2Me})(PPh_3).

Identification code	jul209	
Empirical formula	C25 H26 Au F3 N O4 P S	
Formula weight	721.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21 (No.4)	
Unit cell dimensions	a = 8.3040(1) Å	a= 90°.
	b = 21.4628(5) Å	b= 115.429(1)°.
	c = 8.6563(2) Å	g = 90°.
Volume	1393.32(5) $Å^3$	
Z	2	
Density (calculated)	1.72 Mg/m^3	
Absorption coefficient	5.46 mm^{-1}	
F(000)	704	
Crystal size	0.14 x 0.14 x 0.08 mm^3	

Theta range for data collection	3.42 to 27.49°.
Index ranges	-10<=h<=10, -27<=k<=27, -11<=l<=11
Reflections collected	21466
Independent reflections	6215 [R(int) = 0.047]
Reflections with I>2sigma(I)	5911
Completeness to theta = 27.49°	99.2 %
Absorption correction	Semi-empirical from equivalents
Tmax. and Tmin.	0.5477 and 0.4675
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6215 / 1 / 326
Goodness-of-fit on F^2	0.913
Final R indices [I>2sigma(I)]	R1 = 0.023, wR2 = 0.053
R indices (all data)	R1 = 0.025, wR2 = 0.055
Absolute structure parameter	-0.002(4)
Largest diff. peak and hole	0.56 and -1.25 e.$Å^{-3}$

Data collection KappaCCD , Program package WinGX , Abs correction MULTISCAN
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for jul209. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au	728(1)	2493(1)	2497(1)	21(1)
S	3438(1)	3345(1)	1855(1)	27(1)
P	-207(1)	1577(1)	3020(1)	19(1)
F(1)	5137(4)	2634(1)	4526(4)	59(1)
F(2)	6829(4)	3238(2)	3905(6)	72(1)
F(3)	5233(5)	3608(2)	5093(4)	65(1)

O(1)	1824(8)	4613(2)	4727(7)	56(1)
O(2)	1250(7)	3626(2)	5054(5)	58(1)
O(3)	3849(5)	3948(2)	1413(5)	46(1)
O(4)	3525(5)	2812(2)	902(5)	41(1)
N	1693(4)	3345(2)	2118(5)	24(1)
C(1)	895(6)	3933(2)	2297(6)	29(1)
C(2)	-1164(6)	3904(2)	1248(6)	37(1)
C(3)	-1654(10)	3771(4)	-616(8)	71(2)
C(4)	-2045(9)	4503(3)	1414(9)	54(2)
C(5)	1386(6)	4106(2)	4135(7)	34(1)
C(6)	1744(14)	3762(3)	6847(9)	89(3)
C(7)	5263(7)	3195(2)	3957(7)	41(1)
C(8)	-594(5)	1607(2)	4929(5)	24(1)
C(9)	-1691(7)	1171(2)	5199(7)	41(1)
C(10)	-2012(9)	1211(3)	6631(8)	58(2)
C(11)	-1238(8)	1676(3)	7808(7)	51(1)
C(12)	-135(7)	2110(3)	7555(6)	41(1)
C(13)	191(6)	2070(2)	6124(6)	31(1)
C(14)	1418(5)	975(2)	3307(6)	21(1)
C(15)	1539(8)	437(3)	4286(7)	30(1)
C(16)	2827(8)	-1(2)	4473(7)	45(1)
C(17)	3939(7)	71(2)	3676(7)	41(1)
C(18)	3795(7)	584(3)	2687(7)	42(1)
C(19)	2545(6)	1042(2)	2516(6)	35(1)
C(20)	-2302(5)	1311(2)	1345(5)	22(1)
C(21)	-3719(5)	1723(2)	769(6)	28(1)
C(22)	-5340(6)	1552(3)	-530(6)	41(1)
C(23)	-5546(6)	962(3)	-1279(6)	41(1)
C(24)	-4139(6)	556(2)	-716(6)	36(1)
C(25)	-2516(6)	724(2)	600(6)	27(1)

Table 3. Bond lengths [Å] and angles [°] for jul209.

Au-N	2.079(3)
Au-P	2.2292(10)
S-O(4)	1.430(3)
S-O(3)	1.433(3)
S-N	1.561(3)
S-C(7)	1.829(6)
P-C(14)	1.807(4)
P-C(20)	1.814(4)
P-C(8)	1.815(4)
F(1)-C(7)	1.322(6)
F(2)-C(7)	1.324(6)
F(3)-C(7)	1.333(6)
O(1)-C(5)	1.190(6)
O(2)-C(5)	1.337(6)
O(2)-C(6)	1.454(7)
N-C(1)	1.464(5)
C(1)-C(5)	1.509(7)
C(1)-C(2)	1.556(7)
C(2)-C(3)	1.512(8)
C(2)-C(4)	1.516(7)
C(8)-C(13)	1.379(6)
C(8)-C(9)	1.394(6)
C(9)-C(10)	1.378(7)
C(10)-C(11)	1.373(8)
C(11)-C(12)	1.387(8)
C(12)-C(13)	1.380(6)
C(14)-C(19)	1.383(6)
C(14)-C(15)	1.409(7)
C(15)-C(16)	1.381(7)

C(16)-C(17)	1.378(8)
C(17)-C(18)	1.368(8)
C(18)-C(19)	1.392(7)
C(20)-C(21)	1.382(6)
C(20)-C(25)	1.392(6)
C(21)-C(22)	1.382(6)
C(22)-C(23)	1.399(7)
C(23)-C(24)	1.368(7)
C(24)-C(25)	1.388(7)

N-Au-P	177.47(10)
O(4)-S-O(3)	119.5(2)
O(4)-S-N	111.3(2)
O(3)-S-N	112.4(2)
O(4)-S-C(7)	102.0(2)
O(3)-S-C(7)	103.6(2)
N-S-C(7)	106.3(2)
C(14)-P-C(20)	106.73(19)
C(14)-P-C(8)	108.3(2)
C(20)-P-C(8)	104.73(18)
C(14)-P-Au	110.73(14)
C(20)-P-Au	114.45(13)
C(8)-P-Au	111.53(14)
C(5)-O(2)-C(6)	115.1(5)
C(1)-N-S	120.4(3)
C(1)-N-Au	121.3(3)
S-N-Au	117.90(19)
N-C(1)-C(5)	113.2(4)
N-C(1)-C(2)	109.7(4)
C(5)-C(1)-C(2)	110.9(4)
C(3)-C(2)-C(4)	110.0(5)

C(3)-C(2)-C(1)	110.8(4)
C(4)-C(2)-C(1)	111.4(5)
O(1)-C(5)-O(2)	122.4(5)
O(1)-C(5)-C(1)	125.0(5)
O(2)-C(5)-C(1)	112.6(4)
F(1)-C(7)-F(2)	108.3(4)
F(1)-C(7)-F(3)	107.6(5)
F(2)-C(7)-F(3)	107.9(4)
F(1)-C(7)-S	111.5(3)
F(2)-C(7)-S	111.1(4)
F(3)-C(7)-S	110.3(4)
C(13)-C(8)-C(9)	119.3(4)
C(13)-C(8)-P	119.8(3)
C(9)-C(8)-P	120.9(3)
C(10)-C(9)-C(8)	120.1(5)
C(11)-C(10)-C(9)	120.2(5)
C(10)-C(11)-C(12)	120.0(4)
C(13)-C(12)-C(11)	119.8(5)
C(8)-C(13)-C(12)	120.5(4)
C(19)-C(14)-C(15)	119.7(4)
C(19)-C(14)-P	118.7(3)
C(15)-C(14)-P	121.6(4)
C(16)-C(15)-C(14)	118.7(5)
C(17)-C(16)-C(15)	121.1(5)
C(18)-C(17)-C(16)	120.4(5)
C(17)-C(18)-C(19)	119.8(5)
C(14)-C(19)-C(18)	120.3(4)
C(21)-C(20)-C(25)	119.5(4)
C(21)-C(20)-P	117.6(3)
C(25)-C(20)-P	122.9(3)
C(22)-C(21)-C(20)	120.3(4)

C(21)-C(22)-C(23)	120.0(5)
C(24)-C(23)-C(22)	119.7(4)
C(23)-C(24)-C(25)	120.5(4)
C(24)-C(25)-C(20)	120.0(4)

Triphenylphosphine gold methyl *N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanate (130d)

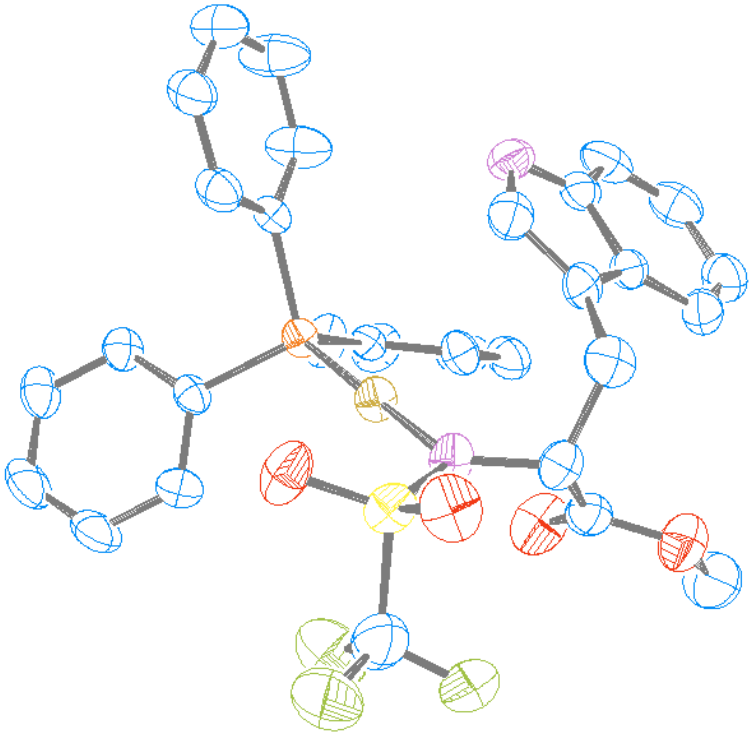


Table 1. Crystal data and structure refinement for import.

Identification code	shelxl
Empirical formula	C37 H33 Au F3 N2 O4 P S
Formula weight	886.65
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 11.5810(2) A alpha = 90 deg.
	b = 13.0950(3) A beta = 114.4260(10) deg.
	c = 13.0305(3) A gamma = 90 deg.
Volume	1799.25(7) A^3
Z, Calculated density	2, 1.637 Mg/m^3
Absorption coefficient	4.248 mm^-1
F(000)	876
Crystal size	0.30 x 0.30 x 0.06 mm

Theta range for data collection	3.43 to 27.26 deg.
Limiting indices	-14<=h<=14, -16<=k<=16, -16<=l<=16
Reflections collected / unique	22995 / 7832 [R(int) = 0.0473]
Completeness to theta = 27.26	98.8 %
Max. and min. transmission	0.7847 and 0.3622
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7832 / 1 / 443
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1194
R indices (all data)	R1 = 0.0519, wR2 = 0.1249
Absolute structure parameter	0.124(9)
Largest diff. peak and hole	2.021 and -2.166 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for import.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	903(6)	2412(6)	8357(5)	48(1)
C(2)	-15(7)	2873(8)	7392(7)	76(3)
C(3)	-1254(6)	2477(13)	6963(7)	81(2)
C(4)	-1543(8)	1659(9)	7459(9)	83(3)
C(5)	-630(10)	1218(7)	8425(11)	81(3)
C(6)	587(8)	1613(6)	8863(7)	64(2)
C(7)	3314(5)	2424(6)	8144(5)	49(1)
C(8)	4562(7)	2686(7)	8478(8)	71(2)
C(9)	5230(9)	2336(7)	7865(10)	82(3)
C(10)	4637(11)	1736(10)	6927(11)	92(3)
C(11)	3383(10)	1453(12)	6613(11)	111(5)

C(12)	2727(9)	1805(10)	7206(10)	95(4)
C(13)	2369(6)	4288(5)	8707(6)	52(2)
C(14)	2251(7)	4701(6)	7697(7)	61(2)
C(15)	2187(9)	5756(7)	7521(9)	77(2)
C(16)	2187(11)	6394(7)	8365(12)	92(3)
C(17)	2259(12)	5996(8)	9349(14)	94(4)
C(18)	2353(9)	4943(7)	9539(8)	69(2)
C(19)	4190(7)	1265(7)	12929(7)	62(2)
C(20)	4547(8)	266(8)	12529(8)	71(2)
C(21)	3962(7)	68(6)	11287(7)	59(2)
C(22)	2778(7)	-444(5)	10628(6)	55(2)
C(23)	2682(9)	-488(7)	9502(7)	60(2)
C(24)	4500(8)	278(7)	10560(9)	73(2)
C(25)	1826(9)	-853(6)	10869(8)	70(2)
C(26)	790(11)	-1291(8)	10006(12)	86(3)
C(27)	689(11)	-1315(8)	8898(10)	88(3)
C(28)	1605(11)	-923(7)	8638(9)	83(3)
C(29)	4950(15)	3708(12)	13902(12)	106(4)
C(30)	2795(9)	1338(7)	12665(8)	68(2)
C(31)	1129(13)	664(12)	13018(14)	116(5)
C(101)	-630(40)	10122(15)	5477(18)	175(12)
C(102)	-1600(20)	9490(20)	5463(19)	152(8)
C(103)	-1450(20)	8470(20)	5410(20)	160(9)
C(104)	-440(30)	8081(17)	5397(17)	156(8)
C(105)	549(16)	8710(30)	5451(14)	187(15)
C(106)	320(30)	9730(30)	5462(18)	174(12)
Au(1)	3547(1)	2531(1)	10771(1)	56(1)
F(1)	4389(12)	3224(7)	14457(9)	150(4)
F(2)	5766(12)	4367(8)	14603(8)	156(4)
F(3)	4029(12)	4275(8)	13141(12)	151(4)
N(1)	4555(6)	2151(5)	12462(4)	62(2)

N(2)	3735(8)	-52(6)	9493(7)	73(2)
O(1)	6550(5)	2309(8)	14176(5)	92(3)
O(2)	6057(7)	3525(7)	12596(6)	94(2)
O(3)	2492(8)	687(7)	13303(8)	95(2)
O(4)	2029(7)	1858(8)	11976(7)	101(2)
P(1)	2500(2)	2931(1)	8963(1)	47(1)
S(5)	5636(2)	2865(2)	13239(2)	67(1)

Table 3. Bond lengths [A] and angles [deg] for import.

C(1)-C(6)	1.365(11)
C(1)-C(2)	1.404(10)
C(1)-P(1)	1.816(7)
C(2)-C(3)	1.406(11)
C(2)-H(2)	0.9300
C(3)-C(4)	1.362(18)
C(3)-H(3)	0.9300
C(4)-C(5)	1.391(16)
C(4)-H(4)	0.9300
C(5)-C(6)	1.383(13)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.370(10)
C(7)-C(12)	1.388(11)
C(7)-P(1)	1.817(6)
C(8)-C(9)	1.399(12)
C(8)-H(8)	0.9300
C(9)-C(10)	1.374(16)
C(9)-H(9)	0.9300
C(10)-C(11)	1.387(16)
C(10)-H(10)	0.9300

C(11)-C(12)	1.368(15)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(14)	1.376(11)
C(13)-C(18)	1.388(11)
C(13)-P(1)	1.803(7)
C(14)-C(15)	1.397(12)
C(14)-H(14)	0.9300
C(15)-C(16)	1.382(16)
C(15)-H(15)	0.9300
C(16)-C(17)	1.354(19)
C(16)-H(16)	0.9300
C(17)-C(18)	1.398(15)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300
C(19)-N(1)	1.452(11)
C(19)-C(30)	1.509(13)
C(19)-C(20)	1.528(14)
C(19)-H(19)	0.9800
C(20)-C(21)	1.496(12)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-C(24)	1.360(12)
C(21)-C(22)	1.447(12)
C(22)-C(25)	1.374(11)
C(22)-C(23)	1.425(11)
C(23)-N(2)	1.351(13)
C(23)-C(28)	1.410(15)
C(24)-N(2)	1.374(13)
C(24)-H(24)	0.9300
C(25)-C(26)	1.385(15)

C(25)-H(25)	0.9300
C(26)-C(27)	1.399(17)
C(26)-H(26)	0.9300
C(27)-C(28)	1.342(17)
C(27)-H(27)	0.9300
C(28)-H(28)	0.9300
C(29)-F(1)	1.317(15)
C(29)-F(2)	1.327(16)
C(29)-F(3)	1.341(19)
C(29)-S(5)	1.778(15)
C(30)-O(4)	1.183(12)
C(30)-O(3)	1.334(12)
C(31)-O(3)	1.465(16)
C(31)-H(31A)	0.9600
C(31)-H(31B)	0.9600
C(31)-H(31C)	0.9600
C(101)-C(106)	1.23(4)
C(101)-C(102)	1.38(4)
C(101)-H(101)	0.9300
C(102)-C(103)	1.35(4)
C(102)-H(102)	0.9300
C(103)-C(104)	1.28(3)
C(103)-H(103)	0.9300
C(104)-C(105)	1.39(4)
C(104)-H(104)	0.9300
C(105)-C(106)	1.35(4)
C(105)-H(105)	0.9300
C(106)-H(106)	0.9300
Au(1)-N(1)	2.084(5)
Au(1)-P(1)	2.2201(16)
N(1)-S(5)	1.555(6)

N(2)-H(2A)	0.8600
O(1)-S(5)	1.440(7)
O(2)-S(5)	1.423(7)
C(6)-C(1)-C(2)	120.5(7)
C(6)-C(1)-P(1)	120.3(5)
C(2)-C(1)-P(1)	119.1(6)
C(1)-C(2)-C(3)	117.9(9)
C(1)-C(2)-H(2)	121.1
C(3)-C(2)-H(2)	121.1
C(4)-C(3)-C(2)	120.8(9)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	120.8(8)
C(3)-C(4)-H(4)	119.6
C(5)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	118.8(10)
C(6)-C(5)-H(5)	120.6
C(4)-C(5)-H(5)	120.6
C(1)-C(6)-C(5)	121.2(8)
C(1)-C(6)-H(6)	119.4
C(5)-C(6)-H(6)	119.4
C(8)-C(7)-C(12)	119.6(7)
C(8)-C(7)-P(1)	117.2(6)
C(12)-C(7)-P(1)	123.2(6)
C(7)-C(8)-C(9)	119.7(8)
C(7)-C(8)-H(8)	120.1
C(9)-C(8)-H(8)	120.1
C(10)-C(9)-C(8)	120.3(9)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(9)-C(10)-C(11)	119.5(10)

C(9)-C(10)-H(10)	120.3
C(11)-C(10)-H(10)	120.3
C(12)-C(11)-C(10)	120.1(10)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(7)	120.7(9)
C(11)-C(12)-H(12)	119.7
C(7)-C(12)-H(12)	119.7
C(14)-C(13)-C(18)	118.5(7)
C(14)-C(13)-P(1)	122.1(6)
C(18)-C(13)-P(1)	119.4(6)
C(13)-C(14)-C(15)	121.5(9)
C(13)-C(14)-H(14)	119.2
C(15)-C(14)-H(14)	119.2
C(16)-C(15)-C(14)	119.0(9)
C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	120.5
C(17)-C(16)-C(15)	120.0(9)
C(17)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
C(16)-C(17)-C(18)	121.2(10)
C(16)-C(17)-H(17)	119.4
C(18)-C(17)-H(17)	119.4
C(13)-C(18)-C(17)	119.7(10)
C(13)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1
N(1)-C(19)-C(30)	108.9(7)
N(1)-C(19)-C(20)	111.9(7)
C(30)-C(19)-C(20)	113.1(7)
N(1)-C(19)-H(19)	107.6
C(30)-C(19)-H(19)	107.6

C(20)-C(19)-H(19)	107.6
C(21)-C(20)-C(19)	116.9(6)
C(21)-C(20)-H(20A)	108.1
C(19)-C(20)-H(20A)	108.1
C(21)-C(20)-H(20B)	108.1
C(19)-C(20)-H(20B)	108.1
H(20A)-C(20)-H(20B)	107.3
C(24)-C(21)-C(22)	105.9(8)
C(24)-C(21)-C(20)	125.8(8)
C(22)-C(21)-C(20)	128.1(7)
C(25)-C(22)-C(23)	119.4(8)
C(25)-C(22)-C(21)	134.2(8)
C(23)-C(22)-C(21)	106.4(7)
N(2)-C(23)-C(28)	131.9(9)
N(2)-C(23)-C(22)	107.8(8)
C(28)-C(23)-C(22)	120.3(9)
C(21)-C(24)-N(2)	110.6(8)
C(21)-C(24)-H(24)	124.7
N(2)-C(24)-H(24)	124.7
C(22)-C(25)-C(26)	118.8(9)
C(22)-C(25)-H(25)	120.6
C(26)-C(25)-H(25)	120.6
C(25)-C(26)-C(27)	121.5(9)
C(25)-C(26)-H(26)	119.3
C(27)-C(26)-H(26)	119.3
C(28)-C(27)-C(26)	121.0(10)
C(28)-C(27)-H(27)	119.5
C(26)-C(27)-H(27)	119.5
C(27)-C(28)-C(23)	118.9(10)
C(27)-C(28)-H(28)	120.6
C(23)-C(28)-H(28)	120.6

F(1)-C(29)-F(2)	107.9(12)
F(1)-C(29)-F(3)	104.6(14)
F(2)-C(29)-F(3)	105.7(14)
F(1)-C(29)-S(5)	112.9(11)
F(2)-C(29)-S(5)	113.8(11)
F(3)-C(29)-S(5)	111.3(10)
O(4)-C(30)-O(3)	122.2(9)
O(4)-C(30)-C(19)	127.2(9)
O(3)-C(30)-C(19)	110.5(8)
O(3)-C(31)-H(31A)	109.5
O(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
O(3)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(106)-C(101)-C(102)	118(2)
C(106)-C(101)-H(101)	120.9
C(102)-C(101)-H(101)	120.9
C(103)-C(102)-C(101)	118(2)
C(103)-C(102)-H(102)	120.9
C(101)-C(102)-H(102)	120.9
C(104)-C(103)-C(102)	122(2)
C(104)-C(103)-H(103)	119.0
C(102)-C(103)-H(103)	119.0
C(103)-C(104)-C(105)	120(2)
C(103)-C(104)-H(104)	120.0
C(105)-C(104)-H(104)	120.0
C(106)-C(105)-C(104)	115.1(18)
C(106)-C(105)-H(105)	122.4
C(104)-C(105)-H(105)	122.4
C(101)-C(106)-C(105)	126(2)

C(101)-C(106)-H(106)	116.8
C(105)-C(106)-H(106)	116.8
N(1)-Au(1)-P(1)	179.1(2)
C(19)-N(1)-S(5)	120.2(5)
C(19)-N(1)-Au(1)	120.1(5)
S(5)-N(1)-Au(1)	119.5(4)
C(23)-N(2)-C(24)	109.3(7)
C(23)-N(2)-H(2A)	125.4
C(24)-N(2)-H(2A)	125.4
C(30)-O(3)-C(31)	112.9(10)
C(13)-P(1)-C(1)	107.2(3)
C(13)-P(1)-C(7)	106.0(4)
C(1)-P(1)-C(7)	106.8(3)
C(13)-P(1)-Au(1)	113.3(3)
C(1)-P(1)-Au(1)	112.6(2)
C(7)-P(1)-Au(1)	110.4(2)
O(2)-S(5)-O(1)	119.7(5)
O(2)-S(5)-N(1)	111.2(4)
O(1)-S(5)-N(1)	111.1(5)
O(2)-S(5)-C(29)	103.9(6)
O(1)-S(5)-C(29)	102.8(6)
N(1)-S(5)-C(29)	106.7(6)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for import.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	50(3)	43(4)	46(3)	-3(3)	17(2)	0(3)

C(2)	47(3)	102(7)	58(4)	19(4)	2(3)	-7(4)
C(3)	44(3)	116(7)	66(4)	-7(8)	6(3)	-15(7)
C(4)	50(4)	112(7)	81(6)	-33(6)	22(4)	-10(4)
C(5)	75(5)	64(5)	114(8)	-12(5)	50(6)	-8(4)
C(6)	63(4)	53(4)	67(5)	6(3)	18(4)	2(3)
C(7)	49(3)	39(3)	51(3)	-3(3)	14(2)	3(3)
C(8)	61(4)	60(6)	89(5)	-18(4)	29(4)	-9(4)
C(9)	65(4)	68(7)	120(7)	-24(5)	46(5)	-13(4)
C(10)	84(7)	102(7)	94(8)	-19(6)	42(6)	6(6)
C(11)	70(6)	152(12)	105(9)	-65(9)	28(6)	-6(6)
C(12)	51(4)	127(9)	90(7)	-54(6)	12(4)	-5(5)
C(13)	43(3)	44(3)	65(4)	-1(3)	18(3)	1(2)
C(14)	56(4)	59(4)	62(4)	11(3)	18(3)	10(3)
C(15)	67(5)	62(5)	97(7)	25(5)	29(5)	12(4)
C(16)	100(7)	45(4)	134(10)	5(5)	50(7)	17(4)
C(17)	96(8)	60(5)	146(12)	-26(7)	70(8)	5(5)
C(18)	71(5)	66(5)	73(5)	-7(4)	31(4)	8(4)
C(19)	57(4)	76(5)	45(4)	12(3)	12(3)	3(3)
C(20)	60(4)	76(5)	61(5)	12(4)	9(3)	18(4)
C(21)	61(4)	53(3)	56(4)	17(3)	19(3)	14(3)
C(22)	65(4)	49(3)	52(4)	13(3)	25(3)	16(3)
C(23)	77(5)	50(4)	55(4)	8(3)	29(4)	17(4)
C(24)	63(4)	69(5)	93(7)	20(4)	39(5)	19(4)
C(25)	75(5)	62(4)	74(5)	9(4)	34(4)	2(4)
C(26)	87(6)	66(5)	116(9)	-12(5)	53(6)	-18(5)
C(27)	81(6)	73(6)	97(8)	-29(5)	24(6)	-8(5)
C(28)	102(8)	63(5)	70(6)	-16(4)	23(5)	14(5)
C(29)	125(10)	112(9)	89(8)	-17(7)	51(8)	-28(8)
C(30)	74(5)	68(4)	64(5)	-9(4)	30(4)	-6(4)
C(31)	98(9)	119(10)	155(14)	-20(10)	77(10)	-26(8)
C(101)	330(40)	98(11)	116(14)	-25(10)	110(20)	-17(18)

C(102)	180(20)	170(20)	111(12)	-1(15)	63(12)	48(17)
C(103)	180(20)	140(17)	210(20)	-47(16)	131(19)	-47(15)
C(104)	220(30)	130(13)	118(13)	15(11)	67(16)	63(16)
C(105)	77(9)	380(50)	68(8)	-43(16)	-2(7)	55(16)
C(106)	210(30)	220(30)	130(16)	-75(19)	111(19)	-110(20)
Au(1)	53(1)	61(1)	38(1)	3(1)	4(1)	-3(1)
F(1)	228(12)	120(6)	176(9)	-19(6)	158(10)	-19(7)
F(2)	223(11)	131(7)	108(6)	-62(6)	62(7)	-64(7)
F(3)	152(9)	111(7)	182(11)	-12(7)	60(8)	19(6)
N(1)	59(3)	76(4)	26(2)	4(2)	-6(2)	-16(3)
N(2)	90(5)	74(4)	64(4)	10(3)	43(4)	18(4)
O(1)	68(3)	105(10)	61(4)	4(3)	-15(3)	-5(3)
O(2)	83(4)	129(6)	65(4)	-5(4)	24(3)	-46(4)
O(3)	91(5)	104(5)	101(5)	15(4)	50(4)	-7(4)
O(4)	60(4)	138(7)	96(5)	25(5)	24(3)	14(4)
P(1)	47(1)	47(1)	37(1)	3(1)	7(1)	1(1)
S(5)	52(1)	92(2)	47(1)	-9(1)	9(1)	-15(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for import.

	x	y	z	U(eq)
H(2)	190	3423	7047	91
H(3)	-1884	2778	6333	97
H(4)	-2360	1393	7149	99
H(5)	-834	667	8770	97
H(6)	1200	1329	9515	77
H(8)	4964	3095	9110	85
H(9)	6078	2511	8093	98

H(10)	5074	1521	6507	110
H(11)	2987	1023	5998	134
H(12)	1879	1628	6977	114
H(14)	2214	4267	7119	73
H(15)	2145	6024	6845	93
H(16)	2138	7098	8258	111
H(17)	2246	6431	9908	113
H(18)	2405	4681	10221	83
H(19)	4656	1295	13751	75
H(20A)	5461	253	12784	85
H(20B)	4320	-293	12897	85
H(24)	5278	600	10758	88
H(25)	1877	-836	11600	84
H(26)	147	-1575	10166	103
H(27)	-24	-1606	8334	106
H(28)	1530	-938	7899	99
H(31A)	965	197	13509	174
H(31B)	680	445	12251	174
H(31C)	848	1335	13105	174
H(101)	-705	10828	5497	210
H(102)	-2327	9759	5486	183
H(103)	-2094	8038	5391	192
H(104)	-372	7377	5349	187
H(105)	1310	8458	5477	224
H(106)	953	10165	5459	209
H(2A)	3900	9	8910	87

Table 6. Torsion angles [deg] for import.

(*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido)propanoate (133e)

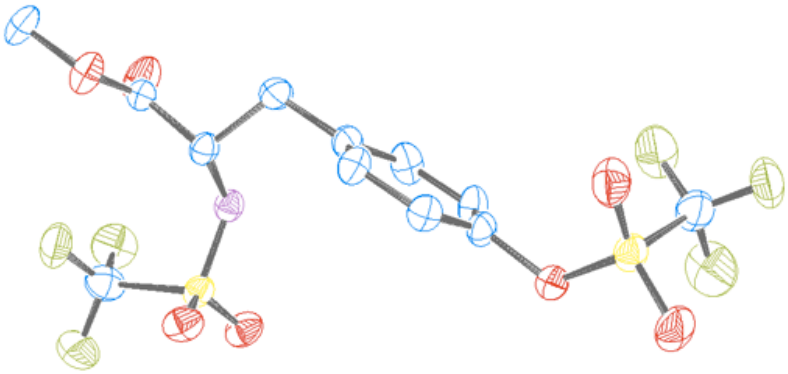


Table 1. Crystal data and structure refinement for import.

Identification code	shelxl
Empirical formula	C12 H10 F6 N O7 S2
Formula weight	458.33
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P1
Unit cell dimensions	a = 8.6306(4) A alpha = 75.784(2) deg.
	b = 10.5975(6) A beta = 68.397(3) deg.
	c = 11.0234(6) A gamma = 84.028(3) deg.
Volume	908.60(8) A^3
Z, Calculated density	2, 1.675 Mg/m^3
Absorption coefficient	0.388 mm^-1
F(000)	462
Crystal size	0.14 x 0.14 x 0.08 mm
Theta range for data collection	2.04 to 27.55 deg.

Limiting indices	-10<=h<=11, -13<=k<=13, -14<=l<=14
Reflections collected / unique	12584 / 7333 [R(int) = 0.0400]
Completeness to theta = 27.55	97.8 %
Max. and min. transmission	0.9696 and 0.9476
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7333 / 3 / 505
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1157
R indices (all data)	R1 = 0.0905, wR2 = 0.1342
Absolute structure parameter	0.03(8)
Largest diff. peak and hole	0.314 and -0.272 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for import.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-2206(8)	-1629(8)	3049(7)	74(2)
C(2)	-672(6)	415(5)	4338(5)	49(1)
C(3)	-259(6)	228(5)	5422(5)	52(1)
C(4)	1293(7)	696(5)	5260(5)	56(1)
C(5)	2312(6)	1358(5)	4020(5)	51(1)
C(6)	1785(8)	1536(6)	2957(5)	64(2)
C(7)	272(7)	1101(6)	3077(5)	60(1)
C(8)	3993(7)	1835(5)	3864(6)	58(1)
C(9)	3815(6)	3178(4)	4263(4)	46(1)
C(10)	5594(6)	3614(5)	3967(6)	51(1)
C(11)	7604(7)	3688(7)	4922(7)	81(2)
C(12)	3050(9)	6507(6)	4017(7)	73(2)

C(51)	13702(10)	9638(8)	9908(7)	83(2)
C(52)	12253(6)	7432(5)	8778(5)	51(1)
C(53)	11231(7)	6831(6)	10005(5)	62(2)
C(54)	9701(7)	6398(6)	10128(5)	64(2)
C(55)	9227(6)	6606(5)	9021(5)	49(1)
C(56)	10333(7)	7204(5)	7789(5)	55(1)
C(57)	11848(7)	7608(6)	7644(5)	59(1)
C(58)	7578(7)	6141(5)	9151(6)	57(1)
C(59)	7408(5)	4667(4)	9487(4)	47(1)
C(60)	5688(6)	4386(5)	9562(5)	51(1)
C(61)	4101(7)	4078(7)	8316(7)	79(2)
C(62)	8500(9)	1493(6)	9068(7)	73(2)
F(1)	-633(5)	-1420(5)	2369(4)	111(2)
F(2)	-2540(5)	-2805(4)	3086(4)	96(1)
F(3)	-3111(7)	-847(5)	2458(4)	122(2)
F(4)	3834(5)	6031(4)	4861(4)	94(1)
F(5)	4159(5)	6869(4)	2811(4)	102(1)
F(6)	2119(5)	7497(4)	4374(5)	106(1)
F(51)	14023(7)	10863(5)	9791(5)	120(2)
F(52)	14506(11)	8958(7)	10619(5)	187(3)
F(53)	12143(7)	9475(7)	10517(6)	185(3)
F(54)	7051(5)	1560(4)	10066(4)	104(1)
F(55)	8163(6)	1616(4)	7975(5)	114(2)
F(56)	9188(6)	370(4)	9344(6)	139(2)
N(1)	3024(4)	4134(4)	3464(3)	49(1)
N(51)	8780(4)	4106(4)	8491(4)	48(1)
O(1)	-1719(6)	-2263(4)	5314(4)	79(1)
O(2)	-4509(5)	-1459(5)	5290(4)	89(1)
O(3)	-2307(4)	45(3)	4472(4)	58(1)
O(4)	5978(5)	3277(4)	5057(4)	71(1)
O(5)	6456(5)	4206(5)	2910(4)	85(1)

O(6)	774(4)	4745(4)	5401(3)	64(1)
O(7)	985(4)	5799(4)	3084(3)	69(1)
O(51)	16131(5)	9270(5)	7834(5)	89(1)
O(52)	13476(6)	10084(4)	7558(5)	86(1)
O(53)	13880(4)	7801(4)	8651(4)	59(1)
O(54)	5682(4)	4291(4)	8394(3)	61(1)
O(55)	4477(4)	4304(4)	10556(3)	69(1)
O(56)	9814(5)	2702(4)	10189(4)	86(1)
O(57)	11239(4)	2724(4)	7779(4)	76(1)
S(1)	-2753(2)	-1405(1)	4739(1)	56(1)
S(2)	1741(1)	5215(1)	4032(1)	50(1)
S(51)	14387(2)	9270(1)	8284(1)	58(1)
S(52)	9793(2)	2820(1)	8896(1)	56(1)

Table 3. Bond lengths [A] and angles [deg] for import.

C(1)-F(2)	1.296(8)
C(1)-F(1)	1.298(7)
C(1)-F(3)	1.303(8)
C(1)-S(1)	1.815(7)
C(2)-C(3)	1.333(7)
C(2)-C(7)	1.385(7)
C(2)-O(3)	1.450(6)
C(3)-C(4)	1.410(7)
C(3)-H(3)	0.9300
C(4)-C(5)	1.381(7)
C(4)-H(4)	0.9300
C(5)-C(6)	1.373(8)
C(5)-C(8)	1.521(7)
C(6)-C(7)	1.379(8)
C(6)-H(6)	0.9300

C(7)-H(7)	0.9300
C(8)-C(9)	1.567(7)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-N(1)	1.459(6)
C(9)-C(10)	1.543(7)
C(9)-H(9)	0.9800
C(10)-O(5)	1.184(6)
C(10)-O(4)	1.319(6)
C(11)-O(4)	1.457(7)
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-F(6)	1.302(7)
C(12)-F(5)	1.311(7)
C(12)-F(4)	1.319(7)
C(12)-S(2)	1.857(7)
C(51)-F(53)	1.271(9)
C(51)-F(52)	1.279(9)
C(51)-F(51)	1.321(9)
C(51)-S(51)	1.795(7)
C(52)-C(53)	1.352(7)
C(52)-C(57)	1.384(7)
C(52)-O(53)	1.444(6)
C(53)-C(54)	1.391(8)
C(53)-H(53)	0.9300
C(54)-C(55)	1.386(7)
C(54)-H(54)	0.9300
C(55)-C(56)	1.381(7)
C(55)-C(58)	1.500(7)
C(56)-C(57)	1.360(8)

C(56)-H(56)	0.9300
C(57)-H(57)	0.9300
C(58)-C(59)	1.524(7)
C(58)-H(58A)	0.9700
C(58)-H(58B)	0.9700
C(59)-N(51)	1.476(6)
C(59)-C(60)	1.514(6)
C(59)-H(59)	0.9800
C(60)-O(55)	1.195(6)
C(60)-O(54)	1.317(5)
C(61)-O(54)	1.442(6)
C(61)-H(61A)	0.9600
C(61)-H(61B)	0.9600
C(61)-H(61C)	0.9600
C(62)-F(56)	1.292(7)
C(62)-F(55)	1.314(8)
C(62)-F(54)	1.337(8)
C(62)-S(52)	1.817(7)
N(1)-S(2)	1.584(4)
N(51)-S(52)	1.600(4)
O(1)-S(1)	1.411(4)
O(2)-S(1)	1.411(4)
O(3)-S(1)	1.554(4)
O(6)-S(2)	1.418(3)
O(7)-S(2)	1.415(4)
O(51)-S(51)	1.400(4)
O(52)-S(51)	1.409(4)
O(53)-S(51)	1.575(4)
O(56)-S(52)	1.407(4)
O(57)-S(52)	1.409(4)
F(2)-C(1)-F(1)	109.1(6)

F(2)-C(1)-F(3)	106.9(6)
F(1)-C(1)-F(3)	110.3(6)
F(2)-C(1)-S(1)	110.0(5)
F(1)-C(1)-S(1)	111.0(5)
F(3)-C(1)-S(1)	109.5(5)
C(3)-C(2)-C(7)	124.6(5)
C(3)-C(2)-O(3)	119.7(5)
C(7)-C(2)-O(3)	115.1(5)
C(2)-C(3)-C(4)	117.8(5)
C(2)-C(3)-H(3)	121.1
C(4)-C(3)-H(3)	121.1
C(5)-C(4)-C(3)	120.4(5)
C(5)-C(4)-H(4)	119.8
C(3)-C(4)-H(4)	119.8
C(6)-C(5)-C(4)	118.4(5)
C(6)-C(5)-C(8)	122.1(5)
C(4)-C(5)-C(8)	119.5(5)
C(5)-C(6)-C(7)	122.9(5)
C(5)-C(6)-H(6)	118.5
C(7)-C(6)-H(6)	118.5
C(6)-C(7)-C(2)	115.8(5)
C(6)-C(7)-H(7)	122.1
C(2)-C(7)-H(7)	122.1
C(5)-C(8)-C(9)	111.3(4)
C(5)-C(8)-H(8A)	109.4
C(9)-C(8)-H(8A)	109.4
C(5)-C(8)-H(8B)	109.4
C(9)-C(8)-H(8B)	109.4
H(8A)-C(8)-H(8B)	108.0
N(1)-C(9)-C(10)	109.7(4)

N(1)-C(9)-C(8)	110.0(4)
C(10)-C(9)-C(8)	106.9(4)
N(1)-C(9)-H(9)	110.1
C(10)-C(9)-H(9)	110.1
C(8)-C(9)-H(9)	110.1
O(5)-C(10)-O(4)	125.6(5)
O(5)-C(10)-C(9)	123.9(5)
O(4)-C(10)-C(9)	110.5(4)
O(4)-C(11)-H(11A)	109.5
O(4)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
O(4)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
F(6)-C(12)-F(5)	110.3(5)
F(6)-C(12)-F(4)	109.7(6)
F(5)-C(12)-F(4)	108.8(6)
F(6)-C(12)-S(2)	110.0(5)
F(5)-C(12)-S(2)	109.2(5)
F(4)-C(12)-S(2)	108.9(4)
F(53)-C(51)-F(52)	110.3(7)
F(53)-C(51)-F(51)	108.0(7)
F(52)-C(51)-F(51)	105.5(7)
F(53)-C(51)-S(51)	111.7(6)
F(52)-C(51)-S(51)	111.2(6)
F(51)-C(51)-S(51)	110.0(5)
C(53)-C(52)-C(57)	122.5(5)
C(53)-C(52)-O(53)	117.8(5)
C(57)-C(52)-O(53)	119.5(5)
C(52)-C(53)-C(54)	118.5(5)
C(52)-C(53)-H(53)	120.8

C(54)-C(53)-H(53)	120.8
C(55)-C(54)-C(53)	120.5(5)
C(55)-C(54)-H(54)	119.7
C(53)-C(54)-H(54)	119.7
C(56)-C(55)-C(54)	118.6(5)
C(56)-C(55)-C(58)	120.7(5)
C(54)-C(55)-C(58)	120.7(5)
C(57)-C(56)-C(55)	121.7(5)
C(57)-C(56)-H(56)	119.1
C(55)-C(56)-H(56)	119.1
C(56)-C(57)-C(52)	118.2(5)
C(56)-C(57)-H(57)	120.9
C(52)-C(57)-H(57)	120.9
C(55)-C(58)-C(59)	115.0(4)
C(55)-C(58)-H(58A)	108.5
C(59)-C(58)-H(58A)	108.5
C(55)-C(58)-H(58B)	108.5
C(59)-C(58)-H(58B)	108.5
H(58A)-C(58)-H(58B)	107.5
N(51)-C(59)-C(60)	114.1(4)
N(51)-C(59)-C(58)	109.6(4)
C(60)-C(59)-C(58)	107.5(4)
N(51)-C(59)-H(59)	108.5
C(60)-C(59)-H(59)	108.5
C(58)-C(59)-H(59)	108.5
O(55)-C(60)-O(54)	124.5(5)
O(55)-C(60)-C(59)	123.6(4)
O(54)-C(60)-C(59)	111.9(4)
O(54)-C(61)-H(61A)	109.5
O(54)-C(61)-H(61B)	109.5
H(61A)-C(61)-H(61B)	109.5

O(54)-C(61)-H(61C)	109.5
H(61A)-C(61)-H(61C)	109.5
H(61B)-C(61)-H(61C)	109.5
F(56)-C(62)-F(55)	110.2(7)
F(56)-C(62)-F(54)	108.5(6)
F(55)-C(62)-F(54)	107.3(6)
F(56)-C(62)-S(52)	111.9(5)
F(55)-C(62)-S(52)	110.5(5)
F(54)-C(62)-S(52)	108.3(5)
C(9)-N(1)-S(2)	123.5(3)
C(59)-N(51)-S(52)	122.7(3)
C(2)-O(3)-S(1)	121.4(3)
C(10)-O(4)-C(11)	115.8(4)
C(52)-O(53)-S(51)	121.9(3)
C(60)-O(54)-C(61)	117.4(4)
O(1)-S(1)-O(2)	122.7(3)
O(1)-S(1)-O(3)	112.4(2)
O(2)-S(1)-O(3)	106.2(3)
O(1)-S(1)-C(1)	106.6(3)
O(2)-S(1)-C(1)	105.0(3)
O(3)-S(1)-C(1)	101.7(3)
O(7)-S(2)-O(6)	121.3(2)
O(7)-S(2)-N(1)	108.4(2)
O(6)-S(2)-N(1)	110.8(2)
O(7)-S(2)-C(12)	104.9(3)
O(6)-S(2)-C(12)	105.1(3)
N(1)-S(2)-C(12)	104.9(3)
O(51)-S(51)-O(52)	122.4(3)
O(51)-S(51)-O(53)	106.0(3)
O(52)-S(51)-O(53)	111.9(2)
O(51)-S(51)-C(51)	105.3(4)

O(52)-S(51)-C(51)	107.4(4)
O(53)-S(51)-C(51)	101.6(3)
O(56)-S(52)-O(57)	123.3(3)
O(56)-S(52)-N(51)	110.3(2)
O(57)-S(52)-N(51)	108.2(2)
O(56)-S(52)-C(62)	104.6(3)
O(57)-S(52)-C(62)	104.5(3)
N(51)-S(52)-C(62)	104.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for import.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	62(4)	93(5)	68(4)	-29(4)	-17(3)	-7(4)
C(2)	43(3)	51(3)	51(3)	-12(2)	-12(2)	-12(2)
C(3)	51(3)	56(3)	45(3)	-6(2)	-13(2)	-8(3)
C(4)	55(3)	61(3)	59(3)	-10(3)	-28(3)	-5(3)
C(5)	45(3)	52(3)	51(3)	-14(2)	-9(2)	-10(3)
C(6)	71(4)	66(4)	46(3)	-12(3)	-3(3)	-26(3)
C(7)	72(4)	66(4)	47(3)	-5(3)	-25(3)	-23(3)
C(8)	42(3)	58(4)	73(4)	-22(3)	-13(3)	-3(3)
C(9)	40(2)	52(3)	44(3)	-8(2)	-12(2)	-10(2)
C(10)	44(3)	53(3)	63(3)	-22(2)	-22(3)	0(2)
C(11)	58(4)	102(5)	107(5)	-28(4)	-54(4)	0(3)
C(12)	74(5)	56(4)	78(4)	-11(3)	-17(4)	-1(3)
C(51)	93(6)	98(6)	51(4)	-15(4)	-9(4)	-32(4)
C(52)	46(3)	52(3)	58(3)	-11(2)	-23(3)	-2(3)
C(53)	73(4)	68(4)	45(3)	-2(3)	-24(3)	-16(3)

C(54)	64(4)	79(4)	43(3)	-11(3)	-8(3)	-27(3)
C(55)	45(3)	48(3)	56(3)	-23(2)	-14(2)	0(2)
C(56)	60(4)	63(3)	44(3)	-6(2)	-20(3)	-14(3)
C(57)	59(4)	68(4)	44(3)	-9(2)	-11(2)	-19(3)
C(58)	41(3)	63(4)	65(3)	-17(3)	-15(3)	0(3)
C(59)	42(2)	57(3)	43(2)	-12(2)	-14(2)	-8(2)
C(60)	51(3)	57(3)	43(3)	-12(2)	-13(2)	-8(2)
C(61)	58(4)	113(5)	82(4)	-32(4)	-35(3)	-10(4)
C(62)	72(5)	61(4)	83(5)	-12(3)	-25(4)	-7(3)
F(1)	85(3)	139(4)	86(3)	-56(2)	26(2)	-46(3)
F(2)	92(3)	99(3)	106(3)	-59(2)	-15(2)	-29(2)
F(3)	165(5)	138(4)	93(3)	-32(3)	-82(3)	19(3)
F(4)	99(3)	97(3)	120(3)	-38(2)	-68(3)	-4(2)
F(5)	90(3)	82(3)	103(3)	2(2)	-6(2)	-35(2)
F(6)	104(3)	75(3)	149(4)	-54(2)	-44(3)	15(2)
F(51)	133(4)	108(3)	129(4)	-64(3)	-27(3)	-26(3)
F(52)	318(10)	177(6)	96(4)	-31(4)	-114(5)	12(6)
F(53)	123(4)	251(7)	151(5)	-143(5)	74(4)	-100(5)
F(54)	83(3)	89(3)	113(3)	-7(2)	-5(2)	-30(2)
F(55)	148(4)	109(3)	113(3)	-49(2)	-58(3)	-21(3)
F(56)	136(4)	59(3)	186(5)	-9(3)	-31(4)	1(2)
N(1)	46(2)	57(2)	44(2)	-11(2)	-15(2)	-7(2)
N(51)	41(2)	55(2)	45(2)	-11(2)	-12(2)	0(2)
O(1)	94(3)	63(3)	93(3)	-11(2)	-50(3)	-12(2)
O(2)	47(2)	129(4)	85(3)	-50(3)	8(2)	-31(2)
O(3)	47(2)	56(2)	74(2)	-21(2)	-20(2)	-4(2)
O(4)	62(2)	90(3)	72(3)	-12(2)	-35(2)	-14(2)
O(5)	58(2)	132(4)	55(2)	-3(2)	-10(2)	-41(2)
O(6)	52(2)	82(3)	44(2)	-5(2)	-5(2)	-2(2)
O(7)	63(2)	90(3)	55(2)	-7(2)	-30(2)	6(2)

O(51)	43(2)	100(3)	108(3)	-34(3)	1(2)	-19(2)
O(52)	110(4)	64(3)	95(3)	2(2)	-60(3)	-1(2)
O(53)	45(2)	62(2)	73(2)	-12(2)	-26(2)	-7(2)
O(54)	41(2)	97(3)	52(2)	-28(2)	-14(2)	-9(2)
O(55)	44(2)	115(3)	47(2)	-25(2)	-7(2)	-12(2)
O(56)	105(3)	100(3)	64(2)	-14(2)	-52(2)	17(2)
O(57)	48(2)	93(3)	73(3)	-18(2)	-9(2)	14(2)
S(1)	46(1)	68(1)	50(1)	-18(1)	-8(1)	-12(1)
S(2)	43(1)	64(1)	42(1)	-10(1)	-14(1)	-4(1)
S(51)	48(1)	63(1)	60(1)	-15(1)	-12(1)	-9(1)
S(52)	51(1)	64(1)	55(1)	-11(1)	-23(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for import.

	x	y	z	U(eq)
H(3)	-970	-197	6257	63
H(4)	1631	557	5992	68
H(6)	2478	1969	2118	77
H(7)	-91	1259	2356	72
H(8A)	4738	1923	2941	70
H(8B)	4479	1198	4424	70
H(9)	3155	3081	5218	55
H(11A)	7766	3395	5764	121
H(11B)	7658	4620	4661	121
H(11C)	8460	3319	4254	121
H(53)	11543	6709	10748	74
H(54)	8990	5966	10960	76
H(56)	10033	7334	7038	66
H(57)	12592	7992	6805	70

H(58A)	7393	6496	8316	68
H(58B)	6708	6489	9844	68
H(59)	7493	4317	10371	56
H(61A)	4261	4026	7421	118
H(61B)	3351	4787	8549	118
H(61C)	3639	3279	8927	118

Table 6. Torsion angles [deg] for import.

Triphenylphosphine gold (*S*)-methyl 3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)-2-(trifluoromethylsulfonamido)propanoate (130e)

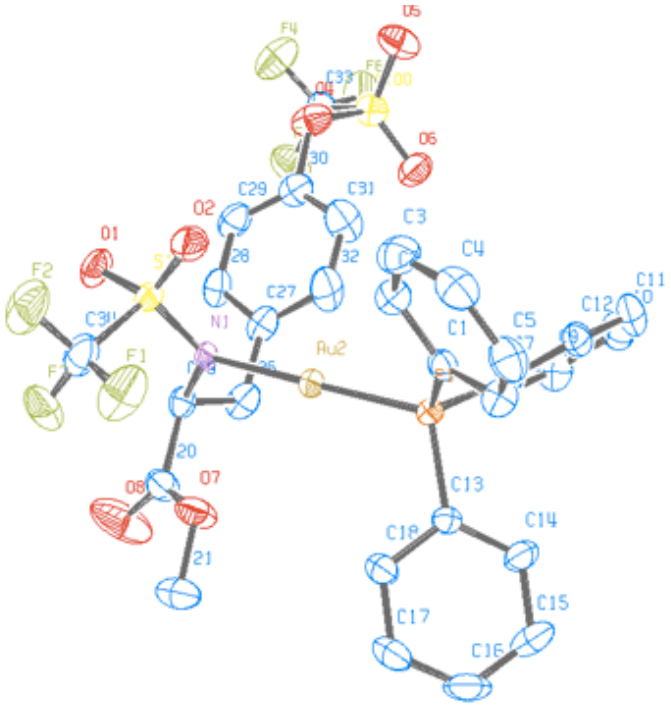


Table 1. Crystal data and structure refinement for import.

Identification code	shelxl
Empirical formula	C30 H25 Au F6 N O7 P S2
Formula weight	917.57
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P 21
Unit cell dimensions	a = 8.69020(10) A alpha = 90 deg.
	b = 34.9283(3) A beta = 103.15 deg.
	c = 11.4932(2) A gamma = 90 deg.
Volume	3397.14(8) A^3
Z, Calculated density	4, 1.794 Mg/m^3
Absorption coefficient	4.579 mm^-1
F(000)	1792
Crystal size	0.20 x 0.20 x 0.10 mm
Theta range for data collection	3.44 to 27.11 deg.

Limiting indices	-11<=h<=11, -44<=k<=44, -14<=l<=14
Reflections collected / unique	32544 / 13530 [R(int) = 0.0551]
Completeness to theta = 27.11	97.7 %
Max. and min. transmission	0.6574 and 0.4611
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13530 / 1 / 865
Goodness-of-fit on F^2	1.003
Final R indices [I>2sigma(I)]	R1 = 0.0375, wR2 = 0.0789
R indices (all data)	R1 = 0.0479, wR2 = 0.0832
Absolute structure parameter	0.050(4)
Largest diff. peak and hole	0.670 and -0.521 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for import.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7842(8)	7092(2)	9324(6)	42(2)
C(2)	6798(9)	7291(2)	9831(7)	53(2)
C(3)	6300(11)	7662(3)	9428(9)	75(3)
C(4)	6914(10)	7822(3)	8530(8)	68(2)
C(5)	7951(11)	7628(2)	8025(7)	65(2)
C(6)	8439(9)	7263(2)	8422(7)	53(2)
C(7)	7424(7)	6266(2)	8903(6)	39(1)
C(8)	7489(9)	5893(2)	9290(7)	51(2)
C(9)	6697(11)	5602(3)	8581(9)	68(2)
C(10)	5777(11)	5695(3)	7477(8)	72(2)
C(11)	5699(11)	6063(3)	7063(7)	70(2)

C(12)	6525(9)	6348(2)	7768(6)	52(2)
C(13)	10527(7)	6572(2)	9790(5)	42(1)
C(14)	10953(9)	6408(2)	8824(7)	57(2)
C(15)	12512(11)	6374(3)	8772(9)	73(3)
C(16)	13643(9)	6500(4)	9704(9)	82(3)
C(17)	13259(9)	6670(4)	10664(8)	85(3)
C(18)	11687(8)	6700(3)	10715(7)	62(2)
C(19)	8653(8)	6152(2)	14238(6)	45(2)
C(20)	10448(9)	6200(3)	14579(7)	59(2)
C(21)	12674(9)	6478(3)	14100(9)	82(3)
C(26)	8251(10)	5770(2)	13604(8)	63(2)
C(27)	6499(10)	5677(2)	13297(7)	55(2)
C(28)	5727(11)	5557(2)	14158(7)	61(2)
C(29)	4117(10)	5466(3)	13886(8)	68(2)
C(30)	3321(10)	5506(2)	12755(8)	61(2)
C(31)	4021(12)	5636(3)	11863(9)	84(3)
C(32)	5605(12)	5716(3)	12146(8)	81(3)
C(33)	627(10)	4760(3)	12860(7)	65(2)
C(34)	8509(12)	7125(3)	14760(9)	75(3)
C(51)	2720(8)	8822(2)	6816(6)	44(2)
C(52)	2222(10)	9039(3)	5805(8)	66(2)
C(53)	3076(13)	9367(3)	5641(11)	90(4)
C(54)	4392(13)	9466(3)	6514(13)	91(4)
C(55)	4907(13)	9247(3)	7460(9)	81(3)
C(56)	4088(10)	8922(3)	7638(7)	62(2)
C(57)	2583(8)	7985(2)	6796(6)	45(2)
C(58)	3381(9)	7988(3)	5860(7)	57(2)
C(59)	4090(11)	7655(3)	5569(8)	77(3)
C(60)	4012(12)	7328(3)	6200(10)	78(3)
C(61)	3230(11)	7325(3)	7100(10)	79(3)
C(62)	2512(9)	7653(3)	7420(8)	61(2)

C(63)	-306(8)	8426(2)	6155(6)	45(1)
C(64)	-1565(8)	8590(2)	6541(7)	52(2)
C(65)	-3017(9)	8611(3)	5746(9)	75(3)
C(66)	-3250(9)	8458(3)	4620(8)	73(2)
C(67)	-2015(10)	8293(3)	4266(8)	78(3)
C(68)	-568(10)	8273(3)	5015(7)	68(2)
C(69)	653(9)	8860(2)	11229(6)	55(2)
C(70)	1195(11)	9241(3)	10782(8)	65(2)
C(71)	2905(11)	9342(2)	11230(8)	61(2)
C(72)	3708(12)	9296(3)	12373(9)	81(3)
C(73)	5285(14)	9392(3)	12759(9)	90(3)
C(74)	6047(12)	9547(3)	11932(10)	76(3)
C(75)	5256(12)	9595(3)	10771(9)	78(3)
C(76)	3696(12)	9499(3)	10396(8)	71(2)
C(77)	-1066(10)	8794(3)	10700(7)	62(2)
C(78)	1116(11)	7840(3)	11831(9)	68(2)
C(84)	8876(18)	10291(4)	12186(12)	103(4)
C(89)	-3492(10)	8610(3)	11082(9)	82(3)
Au(2)	8166(1)	6547(1)	11760(1)	41(1)
Au(51)	1562(1)	8452(1)	9108(1)	46(1)
F(1)	9225(8)	7273(2)	13976(7)	117(3)
F(2)	7878(9)	7409(2)	15234(7)	113(2)
F(3)	9552(7)	6953(2)	15600(6)	115(2)
F(4)	-280(8)	4909(2)	13503(6)	108(2)
F(5)	1941(7)	4662(2)	13578(6)	101(2)
F(6)	-75(9)	4447(2)	12366(6)	105(2)
F(51)	-186(8)	7955(2)	12105(8)	124(3)
F(52)	1763(8)	7577(2)	12607(6)	101(2)
F(53)	767(9)	7678(2)	10766(6)	106(2)
F(54)	7515(13)	10402(3)	11548(9)	159(4)
F(55)	9743(11)	10153(3)	11491(7)	149(3)

F(56)	9700(13)	10558(3)	12806(9)	171(4)
N(1)	7830(6)	6470(2)	13482(4)	37(1)
N(51)	1561(7)	8536(2)	10898(4)	47(2)
O(1)	6401(7)	6646(2)	15026(5)	67(2)
O(2)	5973(7)	7004(2)	13125(5)	73(2)
O(4)	1655(7)	5440(2)	12472(7)	76(2)
O(5)	-591(8)	5190(2)	11078(6)	90(2)
O(6)	2025(7)	4901(2)	11150(6)	75(2)
O(7)	10994(6)	6410(2)	13832(5)	74(2)
O(8)	11252(9)	6060(3)	15440(8)	141(4)
O(51)	3722(7)	8076(2)	11450(7)	88(2)
O(52)	2685(8)	8393(2)	13038(5)	88(2)
O(53)	7747(8)	9605(2)	12245(7)	92(2)
O(54)	10033(11)	9774(3)	13718(9)	143(4)
O(55)	7496(10)	10059(3)	13838(7)	103(3)
O(57)	-1862(6)	8716(2)	11507(5)	70(2)
O(58)	-1673(8)	8804(3)	9654(6)	118(3)
P(1)	8484(2)	6624(1)	9897(2)	38(1)
P(51)	1618(2)	8410(1)	7174(2)	40(1)
S(1)	6971(2)	6784(1)	14034(2)	46(1)
S(51)	2465(2)	8246(1)	11841(2)	55(1)
S(52)	8535(3)	9907(1)	13192(2)	79(1)
S(100)	928(3)	5082(1)	11710(2)	60(1)

Table 3. Bond lengths [A] and angles [deg] for import.

C(1)-C(2)	1.372(10)
C(1)-C(6)	1.394(10)
C(1)-P(1)	1.805(7)
C(2)-C(3)	1.413(12)
C(2)-H(2)	0.9300

C(3)-C(4)	1.382(14)
C(3)-H(3)	0.9300
C(4)-C(5)	1.359(13)
C(4)-H(4)	0.9300
C(5)-C(6)	1.388(11)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.376(10)
C(7)-C(12)	1.389(9)
C(7)-P(1)	1.798(7)
C(8)-C(9)	1.384(12)
C(8)-H(8)	0.9300
C(9)-C(10)	1.376(13)
C(9)-H(9)	0.9300
C(10)-C(11)	1.366(13)
C(10)-H(10)	0.9300
C(11)-C(12)	1.379(11)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(13)-C(18)	1.363(9)
C(13)-C(14)	1.374(9)
C(13)-P(1)	1.817(6)
C(14)-C(15)	1.374(11)
C(14)-H(14)	0.9300
C(15)-C(16)	1.353(13)
C(15)-H(15)	0.9300
C(16)-C(17)	1.360(14)
C(16)-H(16)	0.9300
C(17)-C(18)	1.385(11)
C(17)-H(17)	0.9300
C(18)-H(18)	0.9300

C(19)-N(1)	1.488(9)
C(19)-C(26)	1.523(11)
C(19)-C(20)	1.528(11)
C(19)-H(19)	0.9800
C(20)-O(8)	1.180(10)
C(20)-O(7)	1.297(9)
C(21)-O(7)	1.442(9)
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
C(26)-C(27)	1.518(12)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
C(27)-C(32)	1.380(12)
C(27)-C(28)	1.381(11)
C(28)-C(29)	1.398(12)
C(28)-H(28)	0.9300
C(29)-C(30)	1.334(12)
C(29)-H(29)	0.9300
C(30)-C(31)	1.382(12)
C(30)-O(4)	1.429(10)
C(31)-C(32)	1.369(13)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
C(33)-F(5)	1.294(10)
C(33)-F(4)	1.307(10)
C(33)-F(6)	1.315(10)
C(33)-S(100)	1.800(9)
C(34)-F(3)	1.311(13)
C(34)-F(2)	1.310(11)
C(34)-F(1)	1.313(11)

C(34)-S(1)	1.842(9)
C(51)-C(52)	1.372(11)
C(51)-C(56)	1.384(10)
C(51)-P(51)	1.828(7)
C(52)-C(53)	1.402(14)
C(52)-H(52)	0.9300
C(53)-C(54)	1.383(17)
C(53)-H(53)	0.9300
C(54)-C(55)	1.323(15)
C(54)-H(54)	0.9300
C(55)-C(56)	1.380(12)
C(55)-H(55)	0.9300
C(56)-H(56)	0.9300
C(57)-C(62)	1.373(11)
C(57)-C(58)	1.407(10)
C(57)-P(51)	1.805(7)
C(58)-C(59)	1.393(12)
C(58)-H(58)	0.9300
C(59)-C(60)	1.363(15)
C(59)-H(59)	0.9300
C(60)-C(61)	1.361(14)
C(60)-H(60)	0.9300
C(61)-C(62)	1.394(13)
C(61)-H(61)	0.9300
C(62)-H(62)	0.9300
C(63)-C(68)	1.385(10)
C(63)-C(64)	1.394(10)
C(63)-P(51)	1.811(7)
C(64)-C(65)	1.381(11)
C(64)-H(64)	0.9300
C(65)-C(66)	1.372(13)

C(65)-H(65)	0.9300
C(66)-C(67)	1.360(12)
C(66)-H(66)	0.9300
C(67)-C(68)	1.355(11)
C(67)-H(67)	0.9300
C(68)-H(68)	0.9300
C(69)-N(51)	1.478(10)
C(69)-C(77)	1.497(11)
C(69)-C(70)	1.536(12)
C(69)-H(69)	0.9800
C(70)-C(71)	1.499(13)
C(70)-H(70A)	0.9700
C(70)-H(70B)	0.9700
C(71)-C(72)	1.349(13)
C(71)-C(76)	1.411(13)
C(72)-C(73)	1.382(15)
C(72)-H(72)	0.9300
C(73)-C(74)	1.387(13)
C(73)-H(73)	0.9300
C(74)-C(75)	1.366(13)
C(74)-O(53)	1.453(12)
C(75)-C(76)	1.368(13)
C(75)-H(75)	0.9300
C(76)-H(76)	0.9300
C(77)-O(58)	1.198(10)
C(77)-O(57)	1.307(10)
C(78)-F(51)	1.306(11)
C(78)-F(52)	1.312(11)
C(78)-F(53)	1.320(11)
C(78)-S(51)	1.839(9)

C(84)-F(56)	1.289(14)
C(84)-F(54)	1.302(16)
C(84)-F(55)	1.308(14)
C(84)-S(52)	1.837(14)
C(89)-O(57)	1.437(10)
C(89)-H(89A)	0.9600
C(89)-H(89B)	0.9600
C(89)-H(89C)	0.9600
Au(2)-N(1)	2.083(4)
Au(2)-P(1)	2.2367(17)
Au(51)-N(51)	2.077(5)
Au(51)-P(51)	2.2390(17)
N(1)-S(1)	1.544(6)
N(51)-S(51)	1.559(6)
O(1)-S(1)	1.426(5)
O(2)-S(1)	1.422(6)
O(4)-S(100)	1.572(6)
O(5)-S(100)	1.405(7)
O(6)-S(100)	1.416(6)
O(51)-S(51)	1.405(7)
O(52)-S(51)	1.439(6)
O(53)-S(52)	1.557(7)
O(54)-S(52)	1.384(8)
O(55)-S(52)	1.399(8)
C(2)-C(1)-C(6)	119.7(7)
C(2)-C(1)-P(1)	118.8(6)
C(6)-C(1)-P(1)	121.4(6)
C(1)-C(2)-C(3)	120.5(8)
C(1)-C(2)-H(2)	119.8
C(3)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	118.2(8)

C(4)-C(3)-H(3)	120.9
C(2)-C(3)-H(3)	120.9
C(5)-C(4)-C(3)	121.7(8)
C(5)-C(4)-H(4)	119.2
C(3)-C(4)-H(4)	119.2
C(4)-C(5)-C(6)	120.0(8)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(5)-C(6)-C(1)	119.9(8)
C(5)-C(6)-H(6)	120.0
C(1)-C(6)-H(6)	120.0
C(8)-C(7)-C(12)	118.1(6)
C(8)-C(7)-P(1)	118.4(5)
C(12)-C(7)-P(1)	123.5(5)
C(7)-C(8)-C(9)	121.9(7)
C(7)-C(8)-H(8)	119.1
C(9)-C(8)-H(8)	119.1
C(8)-C(9)-C(10)	118.4(8)
C(8)-C(9)-H(9)	120.8
C(10)-C(9)-H(9)	120.8
C(11)-C(10)-C(9)	121.1(8)
C(11)-C(10)-H(10)	119.4
C(9)-C(10)-H(10)	119.4
C(10)-C(11)-C(12)	119.8(8)
C(10)-C(11)-H(11)	120.1
C(12)-C(11)-H(11)	120.1
C(11)-C(12)-C(7)	120.7(7)
C(11)-C(12)-H(12)	119.7
C(7)-C(12)-H(12)	119.7
C(18)-C(13)-C(14)	118.7(6)
C(18)-C(13)-P(1)	118.4(5)

C(14)-C(13)-P(1)	122.9(5)
C(13)-C(14)-C(15)	121.3(8)
C(13)-C(14)-H(14)	119.3
C(15)-C(14)-H(14)	119.3
C(16)-C(15)-C(14)	118.9(8)
C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	120.5
C(15)-C(16)-C(17)	121.1(7)
C(15)-C(16)-H(16)	119.4
C(17)-C(16)-H(16)	119.4
C(16)-C(17)-C(18)	119.6(8)
C(16)-C(17)-H(17)	120.2
C(18)-C(17)-H(17)	120.2
C(13)-C(18)-C(17)	120.2(8)
C(13)-C(18)-H(18)	119.9
C(17)-C(18)-H(18)	119.9
N(1)-C(19)-C(26)	110.3(6)
N(1)-C(19)-C(20)	113.3(6)
C(26)-C(19)-C(20)	109.2(6)
N(1)-C(19)-H(19)	108.0
C(26)-C(19)-H(19)	108.0
C(20)-C(19)-H(19)	108.0
O(8)-C(20)-O(7)	123.6(8)
O(8)-C(20)-C(19)	123.0(8)
O(7)-C(20)-C(19)	113.4(6)
O(7)-C(21)-H(21A)	109.5
O(7)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
O(7)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5

C(27)-C(26)-C(19)	114.1(7)
C(27)-C(26)-H(26A)	108.7
C(19)-C(26)-H(26A)	108.7
C(27)-C(26)-H(26B)	108.7
C(19)-C(26)-H(26B)	108.7
H(26A)-C(26)-H(26B)	107.6
C(32)-C(27)-C(28)	117.3(8)
C(32)-C(27)-C(26)	121.2(7)
C(28)-C(27)-C(26)	121.6(8)
C(27)-C(28)-C(29)	122.2(8)
C(27)-C(28)-H(28)	118.9
C(29)-C(28)-H(28)	118.9
C(30)-C(29)-C(28)	117.7(8)
C(30)-C(29)-H(29)	121.2
C(28)-C(29)-H(29)	121.2
C(29)-C(30)-C(31)	122.6(8)
C(29)-C(30)-O(4)	118.6(8)
C(31)-C(30)-O(4)	118.6(9)
C(32)-C(31)-C(30)	118.7(9)
C(32)-C(31)-H(31)	120.7
C(30)-C(31)-H(31)	120.7
C(31)-C(32)-C(27)	121.6(8)
C(31)-C(32)-H(32)	119.2
C(27)-C(32)-H(32)	119.2
F(5)-C(33)-F(4)	107.7(8)
F(5)-C(33)-F(6)	108.1(8)
F(4)-C(33)-F(6)	107.2(8)
F(5)-C(33)-S(100)	112.3(6)
F(4)-C(33)-S(100)	111.9(7)
F(6)-C(33)-S(100)	109.5(6)
F(3)-C(34)-F(2)	109.0(8)

F(3)-C(34)-F(1)	109.3(9)
F(2)-C(34)-F(1)	107.3(9)
F(3)-C(34)-S(1)	110.3(7)
F(2)-C(34)-S(1)	110.4(7)
F(1)-C(34)-S(1)	110.6(7)
C(52)-C(51)-C(56)	119.7(7)
C(52)-C(51)-P(51)	123.0(6)
C(56)-C(51)-P(51)	117.2(6)
C(51)-C(52)-C(53)	119.4(9)
C(51)-C(52)-H(52)	120.3
C(53)-C(52)-H(52)	120.3
C(54)-C(53)-C(52)	118.9(10)
C(54)-C(53)-H(53)	120.6
C(52)-C(53)-H(53)	120.6
C(55)-C(54)-C(53)	121.4(10)
C(55)-C(54)-H(54)	119.3
C(53)-C(54)-H(54)	119.3
C(54)-C(55)-C(56)	120.6(10)
C(54)-C(55)-H(55)	119.7
C(56)-C(55)-H(55)	119.7
C(55)-C(56)-C(51)	119.9(9)
C(55)-C(56)-H(56)	120.1
C(51)-C(56)-H(56)	120.1
C(62)-C(57)-C(58)	119.7(7)
C(62)-C(57)-P(51)	119.3(6)
C(58)-C(57)-P(51)	121.0(6)
C(59)-C(58)-C(57)	119.9(9)
C(59)-C(58)-H(58)	120.0
C(57)-C(58)-H(58)	120.0
C(60)-C(59)-C(58)	119.7(9)
C(60)-C(59)-H(59)	120.2

C(58)-C(59)-H(59)	120.2
C(61)-C(60)-C(59)	120.3(8)
C(61)-C(60)-H(60)	119.9
C(59)-C(60)-H(60)	119.9
C(60)-C(61)-C(62)	121.7(9)
C(60)-C(61)-H(61)	119.1
C(62)-C(61)-H(61)	119.1
C(57)-C(62)-C(61)	118.7(8)
C(57)-C(62)-H(62)	120.6
C(61)-C(62)-H(62)	120.6
C(68)-C(63)-C(64)	119.2(7)
C(68)-C(63)-P(51)	121.9(6)
C(64)-C(63)-P(51)	118.9(5)
C(65)-C(64)-C(63)	118.5(7)
C(65)-C(64)-H(64)	120.7
C(63)-C(64)-H(64)	120.7
C(66)-C(65)-C(64)	121.3(8)
C(66)-C(65)-H(65)	119.3
C(64)-C(65)-H(65)	119.3
C(67)-C(66)-C(65)	119.3(7)
C(67)-C(66)-H(66)	120.3
C(65)-C(66)-H(66)	120.3
C(68)-C(67)-C(66)	120.9(8)
C(68)-C(67)-H(67)	119.5
C(66)-C(67)-H(67)	119.5
C(67)-C(68)-C(63)	120.7(8)
C(67)-C(68)-H(68)	119.7
C(63)-C(68)-H(68)	119.7
N(51)-C(69)-C(77)	108.6(6)
N(51)-C(69)-C(70)	110.7(6)

C(77)-C(69)-C(70)	110.5(7)
N(51)-C(69)-H(69)	109.0
C(77)-C(69)-H(69)	109.0
C(70)-C(69)-H(69)	109.0
C(71)-C(70)-C(69)	116.3(7)
C(71)-C(70)-H(70A)	108.2
C(69)-C(70)-H(70A)	108.2
C(71)-C(70)-H(70B)	108.2
C(69)-C(70)-H(70B)	108.2
H(70A)-C(70)-H(70B)	107.4
C(72)-C(71)-C(76)	118.9(9)
C(72)-C(71)-C(70)	124.0(9)
C(76)-C(71)-C(70)	117.1(8)
C(71)-C(72)-C(73)	122.7(10)
C(71)-C(72)-H(72)	118.7
C(73)-C(72)-H(72)	118.7
C(72)-C(73)-C(74)	117.9(10)
C(72)-C(73)-H(73)	121.1
C(74)-C(73)-H(73)	121.1
C(75)-C(74)-C(73)	120.3(9)
C(75)-C(74)-O(53)	118.8(9)
C(73)-C(74)-O(53)	120.2(10)
C(76)-C(75)-C(74)	121.3(9)
C(76)-C(75)-H(75)	119.3
C(74)-C(75)-H(75)	119.3
C(75)-C(76)-C(71)	118.9(9)
C(75)-C(76)-H(76)	120.6
C(71)-C(76)-H(76)	120.6
O(58)-C(77)-O(57)	122.3(8)
O(58)-C(77)-C(69)	125.0(8)
O(57)-C(77)-C(69)	112.6(7)

F(51)-C(78)-F(52)	108.2(8)
F(51)-C(78)-F(53)	109.1(9)
F(52)-C(78)-F(53)	107.7(9)
F(51)-C(78)-S(51)	110.2(7)
F(52)-C(78)-S(51)	111.1(7)
F(53)-C(78)-S(51)	110.4(6)
F(56)-C(84)-F(54)	114.4(13)
F(56)-C(84)-F(55)	106.2(12)
F(54)-C(84)-F(55)	110.0(13)
F(56)-C(84)-S(52)	109.3(10)
F(54)-C(84)-S(52)	108.5(10)
F(55)-C(84)-S(52)	108.3(10)
O(57)-C(89)-H(89A)	109.5
O(57)-C(89)-H(89B)	109.5
H(89A)-C(89)-H(89B)	109.5
O(57)-C(89)-H(89C)	109.5
H(89A)-C(89)-H(89C)	109.5
H(89B)-C(89)-H(89C)	109.5
N(1)-Au(2)-P(1)	178.86(16)
N(51)-Au(51)-P(51)	175.51(19)
C(19)-N(1)-S(1)	120.2(4)
C(19)-N(1)-Au(2)	119.9(4)
S(1)-N(1)-Au(2)	118.9(3)
C(69)-N(51)-S(51)	122.2(4)
C(69)-N(51)-Au(51)	118.9(4)
S(51)-N(51)-Au(51)	118.9(3)
C(30)-O(4)-S(100)	120.9(5)
C(20)-O(7)-C(21)	117.2(7)
C(74)-O(53)-S(52)	122.0(6)
C(77)-O(57)-C(89)	116.9(7)
C(7)-P(1)-C(1)	109.1(3)

C(7)-P(1)-C(13)	104.8(3)
C(1)-P(1)-C(13)	106.9(3)
C(7)-P(1)-Au(2)	111.6(2)
C(1)-P(1)-Au(2)	111.2(2)
C(13)-P(1)-Au(2)	112.8(2)
C(57)-P(51)-C(63)	106.3(4)
C(57)-P(51)-C(51)	107.3(3)
C(63)-P(51)-C(51)	106.5(3)
C(57)-P(51)-Au(51)	114.2(2)
C(63)-P(51)-Au(51)	114.5(2)
C(51)-P(51)-Au(51)	107.6(2)
O(2)-S(1)-O(1)	120.4(4)
O(2)-S(1)-N(1)	110.7(3)
O(1)-S(1)-N(1)	112.1(3)
O(2)-S(1)-C(34)	104.0(5)
O(1)-S(1)-C(34)	101.8(4)
N(1)-S(1)-C(34)	106.1(4)
O(51)-S(51)-O(52)	120.8(5)
O(51)-S(51)-N(51)	110.9(4)
O(52)-S(51)-N(51)	111.7(4)
O(51)-S(51)-C(78)	102.3(5)
O(52)-S(51)-C(78)	103.1(4)
N(51)-S(51)-C(78)	106.1(4)
O(54)-S(52)-O(55)	123.5(6)
O(54)-S(52)-O(53)	107.4(6)
O(55)-S(52)-O(53)	113.2(4)
O(54)-S(52)-C(84)	104.4(7)
O(55)-S(52)-C(84)	105.9(6)
O(53)-S(52)-C(84)	99.3(5)
O(5)-S(100)-O(6)	122.4(5)
O(5)-S(100)-O(4)	106.6(4)

O(6)-S(100)-O(4)	112.5(4)
O(5)-S(100)-C(33)	105.7(4)
O(6)-S(100)-C(33)	106.2(4)
O(4)-S(100)-C(33)	101.2(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for import.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	42(4)	42(4)	41(4)	-5(3)	5(3)	-2(3)
C(2)	55(4)	48(5)	58(5)	-2(3)	15(3)	-4(4)
C(3)	64(5)	72(6)	89(7)	-20(5)	17(5)	8(5)
C(4)	73(6)	47(5)	74(6)	1(4)	-1(4)	6(4)
C(5)	80(6)	53(5)	55(5)	7(4)	3(4)	-2(4)
C(6)	62(5)	43(4)	56(4)	3(3)	17(4)	2(3)
C(7)	35(3)	45(4)	41(3)	-2(3)	13(3)	-7(3)
C(8)	61(5)	46(4)	44(4)	4(3)	10(3)	-7(4)
C(9)	88(7)	50(5)	68(6)	-1(4)	19(5)	-10(4)
C(10)	73(6)	79(7)	63(5)	-22(5)	13(4)	-25(5)
C(11)	83(6)	81(7)	39(4)	2(4)	-1(4)	-9(5)
C(12)	57(4)	58(5)	40(4)	5(3)	6(3)	3(4)
C(13)	34(3)	46(4)	45(3)	-3(3)	10(2)	-2(3)
C(14)	46(4)	68(6)	62(4)	-10(4)	25(3)	-5(4)
C(15)	68(6)	69(6)	99(7)	-9(5)	54(5)	1(4)
C(16)	33(4)	115(8)	99(7)	16(7)	19(4)	0(5)
C(17)	43(4)	136(10)	67(6)	-5(6)	-5(4)	-15(5)
C(18)	42(4)	98(7)	44(4)	1(4)	7(3)	-7(4)
C(19)	56(4)	44(4)	37(3)	4(3)	15(3)	0(3)

C(20)	50(4)	71(6)	53(5)	5(4)	4(4)	-4(4)
C(21)	44(4)	96(8)	100(7)	-1(6)	8(4)	-1(5)
C(26)	75(6)	50(5)	74(6)	-9(4)	34(4)	-9(4)
C(27)	77(5)	33(4)	64(5)	-6(3)	31(4)	-9(4)
C(28)	86(6)	51(5)	50(4)	-7(3)	25(4)	-14(4)
C(29)	74(6)	69(6)	73(6)	-6(4)	39(5)	-11(5)
C(30)	61(5)	43(4)	83(6)	-15(4)	25(4)	-15(4)
C(31)	91(7)	92(8)	67(6)	21(5)	16(5)	-33(6)
C(32)	94(7)	98(8)	56(5)	7(5)	26(5)	-44(6)
C(33)	66(5)	70(6)	55(5)	3(4)	9(4)	1(4)
C(34)	84(7)	70(6)	79(6)	-29(5)	36(6)	-21(5)
C(51)	50(4)	45(4)	40(4)	-5(3)	17(3)	-2(3)
C(52)	54(5)	77(6)	72(5)	19(4)	22(4)	-3(4)
C(53)	79(7)	87(8)	115(9)	51(7)	47(6)	11(6)
C(54)	73(7)	55(6)	156(11)	21(6)	49(7)	-11(5)
C(55)	92(7)	82(7)	75(6)	-17(5)	30(5)	-35(6)
C(56)	63(5)	65(5)	60(5)	-4(4)	19(4)	-17(4)
C(57)	43(4)	44(4)	49(4)	0(3)	12(3)	7(3)
C(58)	52(5)	66(5)	54(5)	-4(4)	15(4)	3(4)
C(59)	77(6)	94(8)	61(5)	-21(5)	17(4)	24(5)
C(60)	75(6)	56(6)	99(7)	-24(5)	11(5)	13(5)
C(61)	79(6)	43(5)	106(8)	9(5)	2(6)	-1(4)
C(62)	60(5)	59(5)	63(5)	14(4)	11(4)	7(4)
C(63)	47(4)	45(4)	47(3)	4(3)	17(3)	0(3)
C(64)	49(4)	60(5)	51(4)	-5(3)	18(3)	2(3)
C(65)	40(4)	89(7)	97(7)	-1(5)	19(4)	17(4)
C(66)	44(4)	95(7)	72(5)	9(6)	-2(4)	5(5)
C(67)	59(5)	117(9)	53(5)	-16(5)	-1(4)	5(5)
C(68)	59(5)	93(7)	51(4)	-8(4)	12(4)	11(4)
C(69)	59(5)	67(5)	40(4)	-5(3)	17(3)	7(4)
C(70)	74(6)	53(5)	69(5)	-5(4)	18(4)	7(4)

C(71)	74(5)	54(5)	58(5)	-12(4)	20(4)	4(4)
C(72)	86(7)	90(8)	65(6)	3(5)	15(5)	-29(6)
C(73)	109(8)	94(8)	62(6)	-5(5)	10(6)	-33(6)
C(74)	77(6)	56(6)	101(8)	-3(5)	33(6)	-10(5)
C(75)	84(7)	87(7)	70(6)	-8(5)	32(5)	-11(6)
C(76)	91(7)	68(6)	57(5)	2(4)	22(5)	-2(5)
C(77)	58(5)	74(6)	53(5)	-8(4)	12(4)	2(4)
C(78)	75(6)	60(6)	72(6)	7(5)	25(5)	-7(5)
C(84)	121(10)	89(9)	102(9)	-20(7)	32(8)	-8(8)
C(89)	62(6)	99(8)	91(7)	-13(6)	27(5)	-7(5)
Au(2)	39(1)	53(1)	32(1)	-2(1)	10(1)	-1(1)
Au(51)	51(1)	53(1)	35(1)	2(1)	16(1)	-1(1)
F(1)	138(6)	94(5)	147(6)	-39(4)	89(5)	-58(4)
F(2)	138(5)	80(4)	136(6)	-57(4)	62(5)	-22(4)
F(3)	83(4)	140(6)	101(5)	-50(4)	-21(3)	-12(4)
F(4)	134(5)	87(4)	126(5)	5(4)	80(4)	7(4)
F(5)	94(4)	107(5)	91(4)	22(4)	-2(3)	6(4)
F(6)	146(6)	72(4)	98(4)	-4(3)	31(4)	-46(4)
F(51)	97(4)	103(5)	198(8)	19(5)	87(5)	-14(4)
F(52)	132(5)	75(4)	93(4)	31(3)	17(4)	-11(4)
F(53)	143(6)	78(4)	87(4)	-14(3)	5(4)	-31(4)
F(54)	190(9)	130(8)	154(8)	47(6)	33(7)	12(7)
F(55)	197(8)	148(7)	138(7)	-59(5)	114(6)	-54(6)
F(56)	241(10)	120(7)	173(9)	-68(6)	89(8)	-80(7)
N(1)	40(3)	51(4)	22(2)	2(2)	11(2)	-5(2)
N(51)	59(3)	58(5)	23(2)	0(2)	10(2)	-2(3)
O(1)	74(4)	81(5)	58(3)	-10(3)	40(3)	-14(3)
O(2)	70(4)	83(4)	63(4)	3(3)	13(3)	30(3)
O(4)	62(4)	54(4)	118(6)	-20(4)	31(3)	-6(3)
O(5)	70(4)	95(5)	95(5)	23(4)	-3(3)	10(4)
O(6)	72(4)	81(5)	78(4)	-12(3)	34(3)	0(3)

O(7)	41(3)	104(5)	71(4)	18(3)	2(3)	-14(3)
O(8)	84(5)	188(10)	128(7)	98(7)	-26(5)	-17(5)
O(51)	53(3)	100(5)	116(5)	41(4)	29(3)	12(3)
O(52)	113(5)	97(5)	43(3)	8(3)	-6(3)	-14(4)
O(53)	83(5)	80(5)	116(6)	-32(4)	30(4)	-12(4)
O(54)	98(6)	183(11)	129(7)	22(7)	-15(5)	35(6)
O(55)	107(6)	134(7)	76(5)	-27(5)	41(4)	-25(5)
O(57)	59(4)	90(5)	67(4)	-2(3)	28(3)	-4(3)
O(58)	76(5)	217(11)	59(4)	8(5)	11(3)	-16(5)
P(1)	34(1)	45(1)	35(1)	0(1)	11(1)	1(1)
P(51)	43(1)	46(1)	34(1)	0(1)	12(1)	1(1)
S(1)	43(1)	57(1)	42(1)	-5(1)	17(1)	-2(1)
S(51)	49(1)	67(1)	45(1)	9(1)	1(1)	-11(1)
S(52)	76(2)	94(2)	64(1)	-1(1)	8(1)	2(1)
S(100)	60(1)	52(1)	67(1)	1(1)	14(1)	-4(1)

Table 5. Torsion angles [deg] for import

N,*N*-dibenzyl-(*D*)-tryptophan (154)

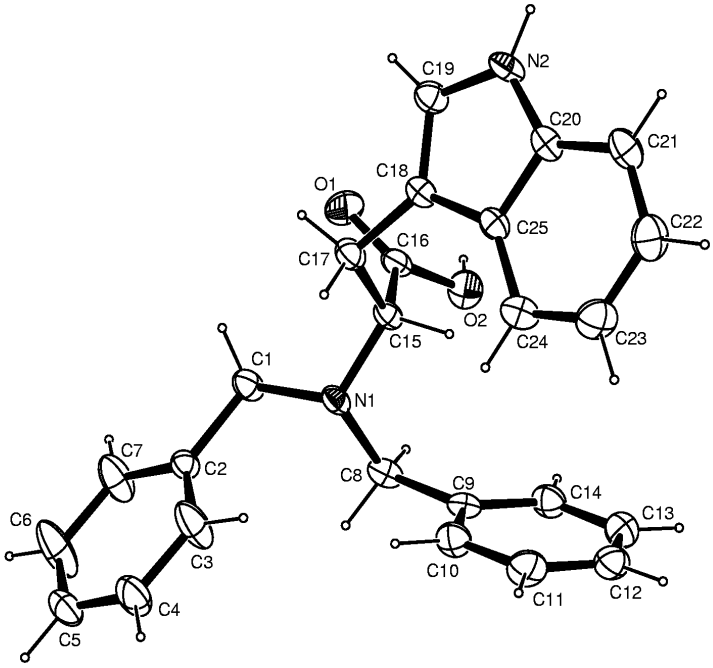


Table 1. Crystal data and structure refinement for $HC(N\{CH_2Ph\}_2)(CH_2C_8NH_6)(CO_2H) \cdot Et_2O$

Identification code	nov309	
Empirical formula	C25 H24 N2 O, C4 H10 O	
Formula weight	458.58	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*P* 2_1 2_1 2_1 (No.19)	
Unit cell dimensions	a = 8.1080(3) Å	a= 90°.
	b = 11.5027(3) Å	b= 90°.
	c = 27.3483(10) Å	g = 90°.
Volume	2550.61(15) $Å^3$	
Z	4	
Density (calculated)	1.19 Mg/m^3	
Absorption coefficient	0.08 mm^{-1}	
F(000)	984	

Crystal size	0.25 x 0.16 x 0.12 mm^3
Theta range for data collection	3.42 to 26.41°.
Index ranges	-8<=h<=10, -12<=k<=14, -30<=l<=34
Reflections collected	12017
Independent reflections	2966 [R(int) = 0.067]
Reflections with I>2sigma(I)	2140
Completeness to theta = 26.41°	99.1 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2966 / 0 / 315
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.049, wR2 = 0.102
R indices (all data)	R1 = 0.084, wR2 = 0.116
Largest diff. peak and hole	0.16 and -0.20 e.$Å^{-3}$

Absolute configuration known only from synthetic sequence

Data collection KappaCCD , Program package WinGX , Abs correction not applied
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for nov309. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	2456(3)	8975(2)	2006(1)	57(1)
O(2)	413(3)	10260(2)	1941(1)	48(1)
O(3)	-1316(3)	9128(2)	2622(1)	49(1)
N(1)	1850(3)	9743(2)	898(1)	32(1)

N(2)	6195(4)	12496(2)	2211(1)	42(1)
C(1)	2138(5)	8476(2)	890(1)	39(1)
C(2)	2033(4)	7971(2)	377(1)	32(1)
C(3)	2285(7)	8624(3)	-35(1)	71(1)
C(4)	2239(6)	8146(3)	-497(1)	65(1)
C(5)	1896(4)	7010(3)	-553(1)	49(1)
C(6)	1646(7)	6354(3)	-152(2)	82(2)
C(7)	1700(6)	6830(3)	313(1)	60(1)
C(8)	121(4)	10036(2)	791(1)	38(1)
C(9)	-73(4)	11312(2)	670(1)	33(1)
C(10)	825(5)	11808(3)	292(1)	44(1)
C(11)	691(5)	12975(3)	184(1)	50(1)
C(12)	-338(4)	13671(3)	454(1)	48(1)
C(13)	-1264(5)	13193(3)	827(1)	49(1)
C(14)	-1119(4)	12022(3)	936(1)	43(1)
C(15)	2511(4)	10337(2)	1335(1)	31(1)
C(16)	1832(4)	9788(3)	1803(1)	36(1)
C(17)	4394(4)	10387(2)	1332(1)	38(1)
C(18)	5036(4)	11394(2)	1626(1)	33(1)
C(19)	5837(4)	11382(3)	2066(1)	39(1)
C(20)	5646(4)	13253(2)	1861(1)	37(1)
C(21)	5728(5)	14464(3)	1842(1)	50(1)
C(22)	5076(5)	14993(3)	1436(1)	58(1)
C(23)	4374(5)	14351(3)	1050(1)	57(1)
C(24)	4271(5)	13164(3)	1074(1)	46(1)
C(25)	4906(4)	12592(2)	1485(1)	34(1)
C(26)	-1703(5)	7955(3)	2484(1)	53(1)
C(27)	-2525(6)	7962(3)	1995(2)	68(1)
C(28)	-673(6)	9189(3)	3110(1)	60(1)
C(29)	-464(7)	10437(4)	3248(2)	82(2)

Table 3. Bond lengths [Å] and angles [°] for nov309.

O(1)-C(16)	1.199(4)
O(2)-C(16)	1.327(4)
O(3)-C(28)	1.434(4)
O(3)-C(26)	1.436(4)
N(1)-C(8)	1.472(4)
N(1)-C(1)	1.476(3)
N(1)-C(15)	1.476(3)
N(2)-C(20)	1.369(4)
N(2)-C(19)	1.372(4)
C(1)-C(2)	1.521(4)
C(2)-C(7)	1.351(4)
C(2)-C(3)	1.369(4)
C(3)-C(4)	1.380(5)
C(4)-C(5)	1.344(5)
C(5)-C(6)	1.347(5)
C(6)-C(7)	1.384(5)
C(8)-C(9)	1.513(4)
C(9)-C(14)	1.385(4)
C(9)-C(10)	1.387(4)
C(10)-C(11)	1.378(4)
C(11)-C(12)	1.372(5)
C(12)-C(13)	1.380(5)
C(13)-C(14)	1.384(4)
C(15)-C(17)	1.528(5)
C(15)-C(16)	1.530(4)
C(17)-C(18)	1.503(4)
C(18)-C(19)	1.366(4)
C(18)-C(25)	1.434(4)
C(20)-C(21)	1.396(4)

C(20)-C(25)	1.411(4)
C(21)-C(22)	1.371(5)
C(22)-C(23)	1.408(5)
C(23)-C(24)	1.370(4)
C(24)-C(25)	1.401(4)
C(26)-C(27)	1.494(5)
C(28)-C(29)	1.494(5)

C(28)-O(3)-C(26)	111.7(2)
C(8)-N(1)-C(1)	112.0(2)
C(8)-N(1)-C(15)	113.6(2)
C(1)-N(1)-C(15)	114.4(2)
C(20)-N(2)-C(19)	108.8(3)
N(1)-C(1)-C(2)	112.5(2)
C(7)-C(2)-C(3)	117.0(3)
C(7)-C(2)-C(1)	120.2(3)
C(3)-C(2)-C(1)	122.8(3)
C(2)-C(3)-C(4)	122.1(3)
C(5)-C(4)-C(3)	119.8(3)
C(4)-C(5)-C(6)	118.9(3)
C(5)-C(6)-C(7)	121.5(3)
C(2)-C(7)-C(6)	120.7(3)
N(1)-C(8)-C(9)	111.4(2)
C(14)-C(9)-C(10)	118.1(3)
C(14)-C(9)-C(8)	121.3(3)
C(10)-C(9)-C(8)	120.6(3)
C(11)-C(10)-C(9)	121.2(3)
C(12)-C(11)-C(10)	120.1(3)
C(11)-C(12)-C(13)	119.7(3)
C(12)-C(13)-C(14)	120.1(3)
C(13)-C(14)-C(9)	120.8(3)

N(1)-C(15)-C(17)	112.1(2)
N(1)-C(15)-C(16)	110.7(2)
C(17)-C(15)-C(16)	112.3(3)
O(1)-C(16)-O(2)	123.6(3)
O(1)-C(16)-C(15)	123.9(3)
O(2)-C(16)-C(15)	112.4(3)
C(18)-C(17)-C(15)	111.9(3)
C(19)-C(18)-C(25)	106.3(2)
C(19)-C(18)-C(17)	128.9(3)
C(25)-C(18)-C(17)	124.9(3)
C(18)-C(19)-N(2)	110.2(3)
N(2)-C(20)-C(21)	130.1(3)
N(2)-C(20)-C(25)	107.7(2)
C(21)-C(20)-C(25)	122.1(3)
C(22)-C(21)-C(20)	117.0(3)
C(21)-C(22)-C(23)	122.0(3)
C(24)-C(23)-C(22)	120.8(3)
C(23)-C(24)-C(25)	118.9(3)
C(24)-C(25)-C(20)	119.2(3)
C(24)-C(25)-C(18)	133.9(3)
C(20)-C(25)-C(18)	106.9(3)
O(3)-C(26)-C(27)	109.2(3)
O(3)-C(28)-C(29)	108.9(3)

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
O2-H1Y	1.011	1.683	164.34	2.670	O3
N2-H1X	0.904	2.086	158.63	2.946	O1 [-x+1, y+1/2, -z+1/2]

(3-((2S)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide (196)

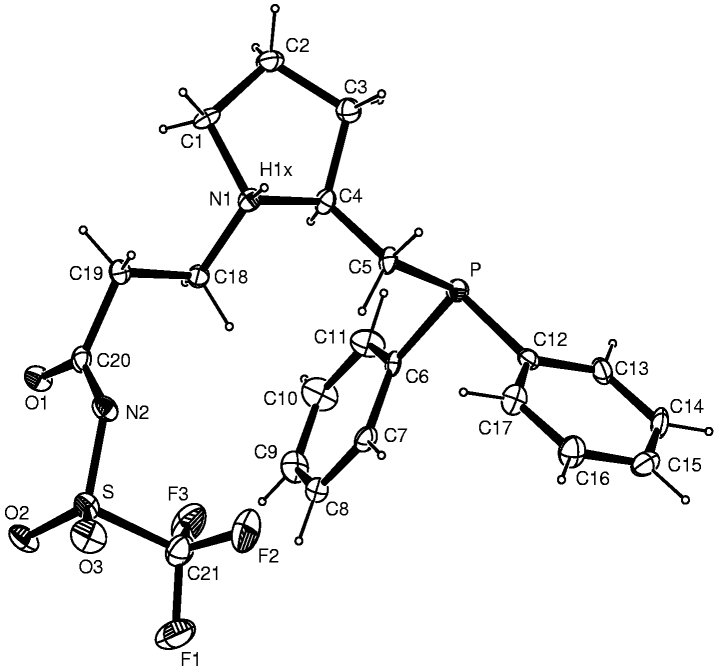


Table 1. Crystal data and structure refinement for jan311.

Identification code	jan311 (2011src0141)	
Empirical formula	C21 H24 F3 N2 O3 P S	
Formula weight	472.45	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$ (No.4)	
Unit cell dimensions	a = 9.5336(5) Å	a= 90°.
	b = 8.6887(3) Å	b= 90.375(2)°.
	c = 13.4224(7) Å	g = 90°.
Volume	1111.82(9) $Å^3$	
Z	2	
Density (calculated)	1.41 Mg/m^3	
Absorption coefficient	0.27 mm^{-1}	
F(000)	492	

Crystal size	0.20 x 0.04 x 0.03 mm^3
Theta range for data collection	3.04 to 27.48°.
Index ranges	-12<=h<=12, -9<=k<=11, -17<=l<=17
Reflections collected	12211
Independent reflections	4711 [R(int) = 0.085]
Reflections with I>2sigma(I)	3295
Completeness to theta = 27.48°	99.3 %
Absorption correction	Semi-empirical from equivalents
Tmax. and Tmin.	0.9920 and 0.8253
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4711 / 1 / 284
Goodness-of-fit on F^2	1.099
Final R indices [I>2sigma(I)]	R1 = 0.084, wR2 = 0.139
R indices (all data)	R1 = 0.135, wR2 = 0.165
Absolute structure parameter	0.26(17)
Largest diff. peak and hole	0.41 and -0.42 e.$Å^{-3}$

NOTE: ANY PUBLICATION THAT INCLUDES THIS DATA MUST ACKNOWLEDGE SERVICE COLLECTION BY THE UK NATIONAL CRYSTALLOGRAPHY SERVICE (NCS) AT THE UNIVERSITY OF SOUTHAMPTON

The hydrogen atom on N1 was located and refined, all others were placed in calculated positions. The data was of insufficient quality to definitvely assign an absolute configuration to the structure.

Data collection Bruker-Nonius APEX II CCD camera on \k-goniostat , Program package WinGX , Abs correction MULTISCAN (sadabs); refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for jan311. U(eq) is defined as one third of the trace of the orthogonalized U^{ij}

tensor.

	x	y	z	U(eq)
S	2463(2)	8037(2)	6476(1)	27(1)
P	4213(2)	8419(2)	826(1)	24(1)
F(1)	51(4)	8768(6)	5677(4)	62(1)
F(2)	1241(5)	7209(6)	4791(4)	71(2)
F(3)	1826(5)	9609(6)	4875(3)	59(1)
O(1)	4935(4)	10075(4)	6103(3)	28(1)
O(2)	2363(5)	9426(5)	7048(4)	36(1)
O(3)	1864(5)	6671(5)	6897(4)	42(1)
N(1)	6589(5)	7693(6)	3341(4)	23(1)
N(2)	3896(5)	7642(5)	5976(4)	27(1)
C(1)	8151(5)	7995(7)	3491(4)	23(1)
C(2)	8799(6)	8001(8)	2453(4)	31(1)
C(3)	7591(6)	7669(7)	1728(4)	28(1)
C(4)	6260(5)	8115(7)	2266(4)	22(1)
C(5)	4920(6)	7338(7)	1902(4)	23(1)
C(6)	3476(6)	10058(7)	1500(4)	20(1)
C(7)	2363(6)	9958(7)	2182(5)	27(1)
C(8)	1873(7)	11255(7)	2673(5)	29(2)
C(9)	2480(7)	12669(7)	2498(5)	36(2)
C(10)	3578(8)	12788(8)	1843(6)	47(2)
C(11)	4073(7)	11492(8)	1356(5)	40(2)
C(12)	2645(6)	7279(7)	503(4)	23(1)
C(13)	2109(7)	7456(8)	-455(4)	30(2)
C(14)	918(7)	6666(8)	-761(5)	34(2)
C(15)	264(7)	5665(8)	-114(6)	36(2)
C(16)	793(7)	5456(8)	841(5)	37(2)
C(17)	1971(7)	6269(7)	1141(5)	32(2)

C(18)	5680(6)	8506(7)	4077(4)	23(1)
C(19)	6069(6)	8117(8)	5151(4)	25(1)
C(20)	4905(6)	8728(7)	5818(4)	24(1)
C(21)	1342(7)	8420(9)	5386(5)	41(2)

Table 3. Bond lengths [Å] and angles [°] for jan311.

S-O(2)	1.434(5)
S-O(3)	1.435(5)
S-N(2)	1.564(5)
S-C(21)	1.837(7)
P-C(6)	1.830(6)
P-C(12)	1.842(6)
P-C(5)	1.847(5)
F(1)-C(21)	1.328(8)
F(2)-C(21)	1.324(8)
F(3)-C(21)	1.325(8)
O(1)-C(20)	1.232(7)
N(1)-C(18)	1.495(8)
N(1)-C(4)	1.520(7)
N(1)-C(1)	1.524(7)
N(2)-C(20)	1.365(7)
C(1)-C(2)	1.528(8)
C(2)-C(3)	1.530(8)
C(3)-C(4)	1.515(8)
C(4)-C(5)	1.522(7)
C(6)-C(11)	1.385(9)
C(6)-C(7)	1.408(9)
C(7)-C(8)	1.388(9)
C(8)-C(9)	1.379(9)
C(9)-C(10)	1.376(10)

C(10)-C(11)	1.386(10)
C(12)-C(17)	1.386(9)
C(12)-C(13)	1.389(8)
C(13)-C(14)	1.387(9)
C(14)-C(15)	1.381(10)
C(15)-C(16)	1.386(10)
C(16)-C(17)	1.384(9)
C(18)-C(19)	1.524(7)
C(19)-C(20)	1.525(8)

O(2)-S-O(3)	117.2(3)
O(2)-S-N(2)	118.4(3)
O(3)-S-N(2)	109.8(3)
O(2)-S-C(21)	103.5(3)
O(3)-S-C(21)	103.4(3)
N(2)-S-C(21)	101.7(3)
C(6)-P-C(12)	102.8(3)
C(6)-P-C(5)	98.5(3)
C(12)-P-C(5)	101.6(3)
C(18)-N(1)-C(4)	113.4(4)
C(18)-N(1)-C(1)	113.7(5)
C(4)-N(1)-C(1)	106.2(4)
C(20)-N(2)-S	122.3(4)
N(1)-C(1)-C(2)	106.3(4)
C(1)-C(2)-C(3)	105.8(5)
C(4)-C(3)-C(2)	106.1(5)
C(3)-C(4)-N(1)	102.9(4)
C(3)-C(4)-C(5)	115.9(5)
N(1)-C(4)-C(5)	111.4(4)
C(4)-C(5)-P	109.1(4)
C(11)-C(6)-C(7)	117.3(6)

C(11)-C(6)-P	118.1(5)
C(7)-C(6)-P	124.6(5)
C(8)-C(7)-C(6)	121.1(6)
C(9)-C(8)-C(7)	119.9(6)
C(10)-C(9)-C(8)	119.9(6)
C(9)-C(10)-C(11)	120.2(6)
C(6)-C(11)-C(10)	121.6(6)
C(17)-C(12)-C(13)	118.2(6)
C(17)-C(12)-P	125.0(4)
C(13)-C(12)-P	116.8(5)
C(14)-C(13)-C(12)	121.0(6)
C(15)-C(14)-C(13)	119.9(6)
C(14)-C(15)-C(16)	120.0(6)
C(17)-C(16)-C(15)	119.5(6)
C(16)-C(17)-C(12)	121.4(6)
N(1)-C(18)-C(19)	112.5(5)
C(18)-C(19)-C(20)	107.7(5)
O(1)-C(20)-N(2)	128.6(6)
O(1)-C(20)-C(19)	119.8(6)
N(2)-C(20)-C(19)	111.6(5)
F(2)-C(21)-F(3)	109.4(6)
F(2)-C(21)-F(1)	107.1(6)
F(3)-C(21)-F(1)	107.5(6)
F(2)-C(21)-S	112.1(5)
F(3)-C(21)-S	110.5(5)
F(1)-C(21)-S	110.1(5)

Bidente Gold(I) complex – dimer (197)

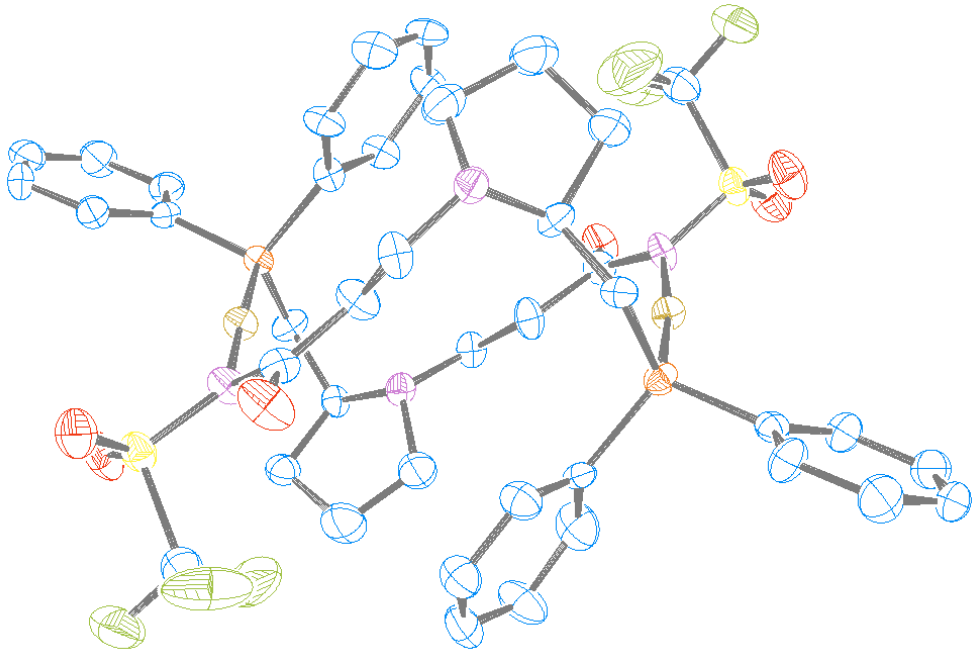


Table 1. Crystal data and structure refinement for import.

Identification code	shelxl
Empirical formula	C72 H72 Au2 F6 N4 O6 P2 S2
Formula weight	1723.33
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P 1
Unit cell dimensions	a = 10.5355(3) A alpha = 94.235(2) deg.
	b = 11.8539(4) A beta = 100.1060(10) deg.
	c = 15.7927(5) A gamma = 112.490(2) deg.
Volume	1772.35(10) A^3
Z, Calculated density	1, 1.615 Mg/m^3
Absorption coefficient	4.307 mm^-1
F(000)	854
Crystal size	0.20 x 0.20 x 0.06 mm
Theta range for data collection	2.13 to 27.51 deg.

Limiting indices	-13<=h<=13, -15<=k<=14, -20<=l<=20
Reflections collected / unique	25196 / 14989 [R(int) = 0.0404]
Completeness to theta = 27.51	98.8 %
Max. and min. transmission	0.7821 and 0.4796
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14989 / 9 / 847
Goodness-of-fit on F^2	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0675
R indices (all data)	R1 = 0.0374, wR2 = 0.0706
Absolute structure parameter	0.006(5)
Largest diff. peak and hole	0.988 and -1.940 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for import. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

x	y	z	U(eq)
C(1)	506(8)	6234(7)	7779(5)	24(2)
C(2)	-800(9)	5319(8)	7358(6)	31(2)
C(3)	-859(8)	4284(7)	6878(6)	36(2)
C(4)	358(10)	4145(8)	6788(6)	40(2)
C(5)	1637(9)	5038(8)	7213(6)	44(2)
C(6)	1742(8)	6088(7)	7707(5)	32(2)
C(7)	1198(10)	7495(8)	9546(6)	26(2)
C(8)	243(10)	6860(10)	10004(7)	45(2)
C(9)	676(10)	6685(10)	10857(7)	45(2)
C(10)	2072(10)	7230(9)	11247(6)	39(2)
C(11)	3038(10)	7891(8)	10805(6)	36(2)
C(12)	2628(10)	8010(8)	9946(6)	33(2)
C(13)	1904(7)	8942(6)	8117(4)	24(1)

C(14)	1548(6)	10093(5)	8277(4)	27(1)
C(15)	859(9)	10381(7)	7413(5)	43(2)
C(16)	1213(8)	11754(7)	7589(5)	48(2)
C(17)	2165(7)	12200(6)	8486(4)	41(2)
C(18)	3484(6)	11373(6)	9521(4)	31(1)
C(19)	2628(9)	11246(9)	10231(6)	35(2)
C(20)	3576(10)	11429(8)	11109(6)	29(2)
C(21)	-438(8)	13899(7)	12164(5)	24(2)
C(22)	-1609(8)	14168(7)	12224(5)	32(2)
C(23)	-1413(10)	15268(8)	12717(6)	42(2)
C(24)	-65(10)	16077(8)	13138(6)	45(2)
C(25)	1078(8)	15822(7)	13087(5)	35(2)
C(26)	878(9)	14709(8)	12586(6)	32(2)
C(27)	-1330(9)	12520(8)	10443(6)	24(2)
C(28)	-2721(9)	12131(8)	10017(6)	32(2)
C(29)	-3083(10)	12309(8)	9165(6)	38(2)
C(30)	-2041(10)	12895(8)	8732(6)	35(2)
C(31)	-630(10)	13301(9)	9143(7)	39(2)
C(32)	-276(9)	13125(8)	9989(6)	30(2)
C(33)	-2205(7)	11321(6)	11971(5)	30(2)
C(34)	-2204(6)	10028(5)	11996(3)	24(1)
C(35)	-1087(7)	9966(6)	12739(4)	31(2)
C(36)	-840(9)	8838(9)	12402(5)	54(2)
C(37)	-1377(8)	8589(7)	11451(4)	49(2)
C(38)	-3087(6)	9082(6)	10458(4)	29(1)
C(39)	-2594(9)	8894(8)	9630(5)	33(2)
C(40)	-3701(9)	8583(8)	8796(6)	27(2)
C(41)	4065(10)	10506(9)	13036(7)	41(2)
C(42)	-3969(11)	9618(10)	6960(7)	44(2)
C(101)	4100(11)	4954(10)	585(8)	61(3)
C(102)	3838(11)	5405(9)	-189(7)	59(3)

C(103)	4787(10)	5590(8)	-737(7)	54(2)
C(104)	5910(11)	5317(9)	-512(7)	54(3)
C(105)	6195(10)	4886(8)	238(7)	51(2)
C(106)	5294(10)	4701(8)	792(6)	52(2)
C(111)	5361(11)	4439(11)	6895(8)	58(3)
C(112)	5566(13)	4502(13)	6075(9)	65(3)
C(113)	5136(15)	3369(14)	5529(9)	74(4)
C(114)	4714(14)	2285(12)	5860(10)	75(4)
C(115)	4537(13)	2295(12)	6681(11)	79(4)
C(116)	4875(10)	3363(11)	7205(8)	58(3)
C(121)	4584(14)	6459(13)	4485(9)	64(3)
C(122)	5191(14)	7624(12)	4266(8)	65(3)
C(123)	5534(11)	7812(10)	3475(8)	56(3)
C(124)	5355(10)	6801(10)	2889(7)	61(3)
C(125)	4821(11)	5624(11)	3101(8)	58(3)
C(126)	4496(13)	5474(10)	3898(8)	56(3)
C(131)	8284(14)	2493(16)	4550(8)	79(4)
C(132)	8138(17)	1512(11)	4961(7)	86(5)
C(133)	9220(20)	1237(12)	5223(8)	88(6)
C(134)	10523(17)	1930(16)	5063(10)	86(5)
C(135)	10680(18)	2922(19)	4660(11)	112(7)
C(136)	9499(15)	3172(13)	4395(7)	69(3)
C(141)	9970(30)	6738(19)	5485(12)	138(10)
C(142)	11380(30)	7330(20)	5479(9)	122(9)
C(143)	11812(13)	8368(19)	5144(10)	112(7)
C(144)	10944(17)	8895(12)	4801(9)	78(4)
C(145)	9595(14)	8331(11)	4814(8)	62(3)
C(146)	9083(19)	7262(14)	5148(11)	96(5)
Au(1)	-1478(1)	7807(1)	8205(1)	26(1)
Au(52)	1233(1)	12052(1)	11728(1)	25(1)
F(1)	2821(7)	9598(6)	12774(6)	88(2)

F(2)	4918(9)	10195(7)	12681(5)	85(2)
F(3)	4455(8)	10588(6)	13885(4)	66(2)
F(4)	-4392(8)	9659(6)	6132(4)	65(2)
F(5)	-2629(8)	10424(7)	7202(7)	102(3)
F(6)	-4698(11)	9999(8)	7393(5)	103(3)
N(1)	-3276(8)	8194(8)	8082(5)	30(2)
N(2)	2741(5)	11265(4)	8629(3)	28(1)
N(3)	3045(8)	11696(8)	11816(5)	27(2)
N(4)	-1894(5)	9525(4)	11202(3)	26(1)
O(1)	-5614(7)	7334(7)	6974(5)	49(2)
O(2)	-3349(8)	7779(7)	6533(5)	44(2)
O(3)	-4792(7)	8670(7)	8773(4)	39(2)
O(4)	3237(8)	12240(7)	13373(4)	48(2)
O(5)	5430(7)	12796(7)	12883(5)	49(2)
O(6)	4683(7)	11289(7)	11201(5)	45(2)
P(1)	572(3)	7601(2)	8409(2)	24(1)
P(52)	-729(2)	12411(2)	11569(2)	21(1)
S(1)	-4145(3)	8043(2)	7110(2)	33(1)
S(51)	4001(3)	11981(2)	12798(2)	32(1)

Table 3. Bond lengths [A] and angles [deg] for import.

C(1)-C(2)	1.394(11)
C(1)-C(6)	1.399(11)
C(1)-P(1)	1.809(9)
C(2)-C(3)	1.368(12)
C(2)-H(2)	0.9500
C(3)-C(4)	1.384(12)
C(3)-H(3)	0.9500
C(4)-C(5)	1.368(12)
C(4)-H(4)	0.9500

C(5)-C(6)	1.376(12)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.363(13)
C(7)-C(12)	1.395(13)
C(7)-P(1)	1.833(9)
C(8)-C(9)	1.401(14)
C(8)-H(8)	0.9500
C(9)-C(10)	1.363(13)
C(9)-H(9)	0.9500
C(10)-C(11)	1.362(13)
C(10)-H(10)	0.9500
C(11)-C(12)	1.385(13)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.562(8)
C(13)-P(1)	1.827(7)
C(14)-N(2)	1.458(7)
C(14)-C(15)	1.554(9)
C(14)-H(14)	1.0000
C(15)-C(16)	1.515(10)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.510(10)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-N(2)	1.466(7)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-N(2)	1.457(7)
C(18)-C(19)	1.539(10)

C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.508(13)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-O(6)	1.225(11)
C(20)-N(3)	1.400(11)
C(21)-C(26)	1.360(11)
C(21)-C(22)	1.404(11)
C(21)-P(52)	1.825(8)
C(22)-C(23)	1.392(12)
C(22)-H(22)	0.9500
C(23)-C(24)	1.382(12)
C(23)-H(23)	0.9500
C(24)-C(25)	1.362(13)
C(24)-H(24)	0.9500
C(25)-C(26)	1.410(12)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(27)-C(28)	1.380(12)
C(27)-C(32)	1.417(11)
C(27)-P(52)	1.811(9)
C(28)-C(29)	1.387(12)
C(28)-H(28)	0.9500
C(29)-C(30)	1.380(12)
C(29)-H(29)	0.9500
C(30)-C(31)	1.389(13)
C(30)-H(30)	0.9500
C(31)-C(32)	1.376(13)
C(31)-H(31)	0.9500
C(32)-H(32)	0.9500

C(33)-C(34)	1.536(8)
C(33)-P(52)	1.850(7)
C(34)-N(4)	1.489(6)
C(34)-C(35)	1.536(9)
C(34)-H(34)	1.0000
C(35)-C(36)	1.532(9)
C(35)-H(35A)	0.9900
C(35)-H(35B)	0.9900
C(36)-C(37)	1.475(10)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-N(4)	1.460(7)
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-N(4)	1.457(7)
C(38)-C(39)	1.521(9)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
C(39)-C(40)	1.514(12)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-O(3)	1.187(11)
C(40)-N(1)	1.394(12)
C(41)-F(2)	1.287(11)
C(41)-F(1)	1.309(11)
C(41)-F(3)	1.317(11)
C(41)-S(51)	1.838(10)
C(42)-F(6)	1.290(12)
C(42)-F(4)	1.316(11)
C(42)-F(5)	1.333(12)
C(42)-S(1)	1.842(10)

C(101)-C(106)	1.392(15)
C(101)-C(102)	1.395(16)
C(101)-H(101)	0.9500
C(102)-C(103)	1.401(16)
C(102)-H(102)	0.9500
C(103)-C(104)	1.340(15)
C(103)-H(103)	0.9500
C(104)-C(105)	1.355(15)
C(104)-H(104)	0.9500
C(105)-C(106)	1.368(15)
C(105)-H(105)	0.9500
C(106)-H(106)	0.9500
C(111)-C(116)	1.345(16)
C(111)-C(112)	1.353(17)
C(111)-H(111)	0.9500
C(112)-C(113)	1.41(2)
C(112)-H(112)	0.9500
C(113)-C(114)	1.37(2)
C(113)-H(113)	0.9500
C(114)-C(115)	1.34(2)
C(114)-H(114)	0.9500
C(115)-C(116)	1.346(18)
C(115)-H(115)	0.9500
C(116)-H(116)	0.9500
C(121)-C(122)	1.382(19)
C(121)-C(126)	1.399(18)
C(121)-H(121)	0.9500
C(122)-C(123)	1.370(17)
C(122)-H(122)	0.9500
C(123)-C(124)	1.389(16)
C(123)-H(123)	0.9500

C(124)-C(125)	1.381(15)
C(124)-H(124)	0.9500
C(125)-C(126)	1.368(16)
C(125)-H(125)	0.9500
C(126)-H(126)	0.9500
C(131)-C(136)	1.30(2)
C(131)-C(132)	1.34(2)
C(131)-H(131)	0.9500
C(132)-C(133)	1.31(2)
C(132)-H(132)	0.9500
C(133)-C(134)	1.38(2)
C(133)-H(133)	0.9500
C(134)-C(135)	1.35(2)
C(134)-H(134)	0.9500
C(135)-C(136)	1.39(2)
C(135)-H(135)	0.9500
C(136)-H(136)	0.9500
C(141)-C(146)	1.36(3)
C(141)-C(142)	1.39(3)
C(141)-H(141)	0.9500
C(142)-C(143)	1.32(3)
C(142)-H(142)	0.9500
C(143)-C(144)	1.35(2)
C(143)-H(143)	0.9500
C(144)-C(145)	1.324(19)
C(144)-H(144)	0.9500
C(145)-C(146)	1.360(18)
C(145)-H(145)	0.9500
C(146)-H(146)	0.9500
Au(1)-N(1)	2.094(8)
Au(1)-P(1)	2.236(3)

Au(52)-N(3)	2.091(7)
Au(52)-P(52)	2.242(2)
N(1)-S(1)	1.601(8)
N(3)-S(51)	1.627(8)
O(1)-S(1)	1.418(8)
O(2)-S(1)	1.436(7)
O(4)-S(51)	1.405(8)
O(5)-S(51)	1.419(7)

C(2)-C(1)-C(6)	119.9(8)
C(2)-C(1)-P(1)	119.0(6)
C(6)-C(1)-P(1)	121.0(6)
C(3)-C(2)-C(1)	119.4(8)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	121.0(7)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(5)-C(4)-C(3)	119.3(8)
C(5)-C(4)-H(4)	120.4
C(3)-C(4)-H(4)	120.4
C(4)-C(5)-C(6)	121.5(8)
C(4)-C(5)-H(5)	119.2
C(6)-C(5)-H(5)	119.2
C(5)-C(6)-C(1)	118.8(7)
C(5)-C(6)-H(6)	120.6
C(1)-C(6)-H(6)	120.6
C(8)-C(7)-C(12)	119.2(9)
C(8)-C(7)-P(1)	119.0(8)
C(12)-C(7)-P(1)	121.8(7)
C(7)-C(8)-C(9)	121.2(9)

C(7)-C(8)-H(8)	119.4
C(9)-C(8)-H(8)	119.4
C(10)-C(9)-C(8)	118.7(9)
C(10)-C(9)-H(9)	120.6
C(8)-C(9)-H(9)	120.6
C(11)-C(10)-C(9)	120.7(9)
C(11)-C(10)-H(10)	119.6
C(9)-C(10)-H(10)	119.6
C(10)-C(11)-C(12)	120.9(9)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-H(11)	119.6
C(11)-C(12)-C(7)	119.1(9)
C(11)-C(12)-H(12)	120.4
C(7)-C(12)-H(12)	120.4
C(14)-C(13)-P(1)	109.4(4)
N(2)-C(14)-C(15)	102.1(5)
N(2)-C(14)-C(13)	116.2(5)
C(15)-C(14)-C(13)	111.7(6)
N(2)-C(14)-H(14)	108.8
C(15)-C(14)-H(14)	108.8
C(13)-C(14)-H(14)	108.8
C(16)-C(15)-C(14)	104.5(6)
C(16)-C(15)-H(15A)	110.8
C(14)-C(15)-H(15A)	110.8
C(16)-C(15)-H(15B)	110.8
C(14)-C(15)-H(15B)	110.8
H(15A)-C(15)-H(15B)	108.9
C(17)-C(16)-C(15)	105.3(5)
C(17)-C(16)-H(16A)	110.7
C(15)-C(16)-H(16A)	110.7
C(17)-C(16)-H(16B)	110.7

C(15)-C(16)-H(16B)	110.7
H(16A)-C(16)-H(16B)	108.8
N(2)-C(17)-C(16)	104.7(5)
N(2)-C(17)-H(17A)	110.8
C(16)-C(17)-H(17A)	110.8
N(2)-C(17)-H(17B)	110.8
C(16)-C(17)-H(17B)	110.8
H(17A)-C(17)-H(17B)	108.9
N(2)-C(18)-C(19)	117.0(5)
N(2)-C(18)-H(18A)	108.0
C(19)-C(18)-H(18A)	108.0
N(2)-C(18)-H(18B)	108.0
C(19)-C(18)-H(18B)	108.0
H(18A)-C(18)-H(18B)	107.3
C(20)-C(19)-C(18)	109.5(6)
C(20)-C(19)-H(19A)	109.8
C(18)-C(19)-H(19A)	109.8
C(20)-C(19)-H(19B)	109.8
C(18)-C(19)-H(19B)	109.8
H(19A)-C(19)-H(19B)	108.2
O(6)-C(20)-N(3)	122.6(9)
O(6)-C(20)-C(19)	122.9(8)
N(3)-C(20)-C(19)	114.4(8)
C(26)-C(21)-C(22)	120.2(8)
C(26)-C(21)-P(52)	121.0(7)
C(22)-C(21)-P(52)	118.7(6)
C(23)-C(22)-C(21)	119.5(7)
C(23)-C(22)-H(22)	120.2
C(21)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	119.2(8)
C(24)-C(23)-H(23)	120.4

C(22)-C(23)-H(23)	120.4
C(25)-C(24)-C(23)	121.8(8)
C(25)-C(24)-H(24)	119.1
C(23)-C(24)-H(24)	119.1
C(24)-C(25)-C(26)	119.0(8)
C(24)-C(25)-H(25)	120.5
C(26)-C(25)-H(25)	120.5
C(21)-C(26)-C(25)	120.4(8)
C(21)-C(26)-H(26)	119.8
C(25)-C(26)-H(26)	119.8
C(28)-C(27)-C(32)	118.0(8)
C(28)-C(27)-P(52)	125.2(7)
C(32)-C(27)-P(52)	116.7(6)
C(27)-C(28)-C(29)	121.2(8)
C(27)-C(28)-H(28)	119.4
C(29)-C(28)-H(28)	119.4
C(30)-C(29)-C(28)	119.9(9)
C(30)-C(29)-H(29)	120.1
C(28)-C(29)-H(29)	120.1
C(29)-C(30)-C(31)	120.4(9)
C(29)-C(30)-H(30)	119.8
C(31)-C(30)-H(30)	119.8
C(32)-C(31)-C(30)	119.5(8)
C(32)-C(31)-H(31)	120.2
C(30)-C(31)-H(31)	120.2
C(31)-C(32)-C(27)	121.0(8)
C(31)-C(32)-H(32)	119.5
C(27)-C(32)-H(32)	119.5
C(34)-C(33)-P(52)	114.5(4)
N(4)-C(34)-C(33)	113.5(5)
N(4)-C(34)-C(35)	103.3(5)

C(33)-C(34)-C(35)	114.4(5)
N(4)-C(34)-H(34)	108.4
C(33)-C(34)-H(34)	108.4
C(35)-C(34)-H(34)	108.4
C(36)-C(35)-C(34)	103.8(5)
C(36)-C(35)-H(35A)	111.0
C(34)-C(35)-H(35A)	111.0
C(36)-C(35)-H(35B)	111.0
C(34)-C(35)-H(35B)	111.0
H(35A)-C(35)-H(35B)	109.0
C(37)-C(36)-C(35)	106.5(6)
C(37)-C(36)-H(36A)	110.4
C(35)-C(36)-H(36A)	110.4
C(37)-C(36)-H(36B)	110.4
C(35)-C(36)-H(36B)	110.4
H(36A)-C(36)-H(36B)	108.6
N(4)-C(37)-C(36)	108.4(5)
N(4)-C(37)-H(37A)	110.0
C(36)-C(37)-H(37A)	110.0
N(4)-C(37)-H(37B)	110.0
C(36)-C(37)-H(37B)	110.0
H(37A)-C(37)-H(37B)	108.4
N(4)-C(38)-C(39)	109.7(5)
N(4)-C(38)-H(38A)	109.7
C(39)-C(38)-H(38A)	109.7
N(4)-C(38)-H(38B)	109.7
C(39)-C(38)-H(38B)	109.7
H(38A)-C(38)-H(38B)	108.2
C(40)-C(39)-C(38)	114.8(7)
C(40)-C(39)-H(39A)	108.6
C(38)-C(39)-H(39A)	108.6

C(40)-C(39)-H(39B)	108.6
C(38)-C(39)-H(39B)	108.6
H(39A)-C(39)-H(39B)	107.5
O(3)-C(40)-N(1)	125.4(9)
O(3)-C(40)-C(39)	122.7(8)
N(1)-C(40)-C(39)	111.9(7)
F(2)-C(41)-F(1)	106.7(10)
F(2)-C(41)-F(3)	108.0(9)
F(1)-C(41)-F(3)	107.9(9)
F(2)-C(41)-S(51)	114.8(7)
F(1)-C(41)-S(51)	110.9(7)
F(3)-C(41)-S(51)	108.4(7)
F(6)-C(42)-F(4)	107.8(9)
F(6)-C(42)-F(5)	108.1(10)
F(4)-C(42)-F(5)	106.6(9)
F(6)-C(42)-S(1)	112.6(8)
F(4)-C(42)-S(1)	110.2(7)
F(5)-C(42)-S(1)	111.2(7)
C(106)-C(101)-C(102)	119.3(11)
C(106)-C(101)-H(101)	120.4
C(102)-C(101)-H(101)	120.4
C(101)-C(102)-C(103)	118.9(10)
C(101)-C(102)-H(102)	120.6
C(103)-C(102)-H(102)	120.6
C(104)-C(103)-C(102)	119.4(10)
C(104)-C(103)-H(103)	120.3
C(102)-C(103)-H(103)	120.3
C(103)-C(104)-C(105)	123.0(10)
C(103)-C(104)-H(104)	118.5
C(105)-C(104)-H(104)	118.5
C(104)-C(105)-C(106)	119.2(10)

C(104)-C(105)-H(105)	120.4
C(106)-C(105)-H(105)	120.4
C(105)-C(106)-C(101)	120.3(10)
C(105)-C(106)-H(106)	119.9
C(101)-C(106)-H(106)	119.9
C(116)-C(111)-C(112)	122.6(13)
C(116)-C(111)-H(111)	118.7
C(112)-C(111)-H(111)	118.7
C(111)-C(112)-C(113)	116.5(13)
C(111)-C(112)-H(112)	121.8
C(113)-C(112)-H(112)	121.8
C(114)-C(113)-C(112)	120.3(13)
C(114)-C(113)-H(113)	119.8
C(112)-C(113)-H(113)	119.8
C(115)-C(114)-C(113)	119.3(13)
C(115)-C(114)-H(114)	120.4
C(113)-C(114)-H(114)	120.4
C(114)-C(115)-C(116)	121.2(12)
C(114)-C(115)-H(115)	119.4
C(116)-C(115)-H(115)	119.4
C(111)-C(116)-C(115)	119.6(12)
C(111)-C(116)-H(116)	120.2
C(115)-C(116)-H(116)	120.2
C(122)-C(121)-C(126)	116.2(12)
C(122)-C(121)-H(121)	121.9
C(126)-C(121)-H(121)	121.9
C(123)-C(122)-C(121)	122.6(12)
C(123)-C(122)-H(122)	118.7
C(121)-C(122)-H(122)	118.7
C(122)-C(123)-C(124)	119.0(11)
C(122)-C(123)-H(123)	120.5

C(124)-C(123)-H(123)	120.5
C(125)-C(124)-C(123)	120.1(11)
C(125)-C(124)-H(124)	119.9
C(123)-C(124)-H(124)	119.9
C(126)-C(125)-C(124)	119.1(11)
C(126)-C(125)-H(125)	120.4
C(124)-C(125)-H(125)	120.4
C(125)-C(126)-C(121)	122.4(11)
C(125)-C(126)-H(126)	118.8
C(121)-C(126)-H(126)	118.8
C(136)-C(131)-C(132)	120.5(14)
C(136)-C(131)-H(131)	119.8
C(132)-C(131)-H(131)	119.8
C(133)-C(132)-C(131)	120.5(14)
C(133)-C(132)-H(132)	119.8
C(131)-C(132)-H(132)	119.8
C(132)-C(133)-C(134)	120.7(12)
C(132)-C(133)-H(133)	119.7
C(134)-C(133)-H(133)	119.7
C(135)-C(134)-C(133)	119.1(14)
C(135)-C(134)-H(134)	120.4
C(133)-C(134)-H(134)	120.4
C(134)-C(135)-C(136)	117.8(14)
C(134)-C(135)-H(135)	121.1
C(136)-C(135)-H(135)	121.1
C(131)-C(136)-C(135)	121.4(14)
C(131)-C(136)-H(136)	119.3
C(135)-C(136)-H(136)	119.3
C(146)-C(141)-C(142)	117.9(16)
C(146)-C(141)-H(141)	121.0
C(142)-C(141)-H(141)	121.0

C(143)-C(142)-C(141)	119.0(15)
C(143)-C(142)-H(142)	120.5
C(141)-C(142)-H(142)	120.5
C(142)-C(143)-C(144)	123.7(15)
C(142)-C(143)-H(143)	118.1
C(144)-C(143)-H(143)	118.1
C(145)-C(144)-C(143)	117.1(15)
C(145)-C(144)-H(144)	121.4
C(143)-C(144)-H(144)	121.4
C(144)-C(145)-C(146)	122.2(15)
C(144)-C(145)-H(145)	118.9
C(146)-C(145)-H(145)	118.9
C(145)-C(146)-C(141)	120.0(17)
C(145)-C(146)-H(146)	120.0
C(141)-C(146)-H(146)	120.0
N(1)-Au(1)-P(1)	173.9(2)
N(3)-Au(52)-P(52)	177.4(2)
C(40)-N(1)-S(1)	120.8(7)
C(40)-N(1)-Au(1)	122.8(6)
S(1)-N(1)-Au(1)	116.4(4)
C(18)-N(2)-C(14)	116.0(5)
C(18)-N(2)-C(17)	114.4(5)
C(14)-N(2)-C(17)	104.3(5)
C(20)-N(3)-S(51)	119.3(6)
C(20)-N(3)-Au(52)	125.5(6)
S(51)-N(3)-Au(52)	114.5(4)
C(38)-N(4)-C(37)	114.1(5)
C(38)-N(4)-C(34)	112.9(4)
C(37)-N(4)-C(34)	106.6(5)
C(1)-P(1)-C(13)	107.7(3)
C(1)-P(1)-C(7)	105.4(4)

C(13)-P(1)-C(7)	108.1(4)
C(1)-P(1)-Au(1)	114.3(3)
C(13)-P(1)-Au(1)	109.5(2)
C(7)-P(1)-Au(1)	111.7(3)
C(27)-P(52)-C(21)	104.1(4)
C(27)-P(52)-C(33)	109.9(4)
C(21)-P(52)-C(33)	102.5(3)
C(27)-P(52)-Au(52)	110.2(3)
C(21)-P(52)-Au(52)	112.8(3)
C(33)-P(52)-Au(52)	116.6(2)
O(1)-S(1)-O(2)	120.5(5)
O(1)-S(1)-N(1)	114.7(4)
O(2)-S(1)-N(1)	106.8(4)
O(1)-S(1)-C(42)	105.2(5)
O(2)-S(1)-C(42)	103.3(5)
N(1)-S(1)-C(42)	104.7(5)
O(4)-S(51)-O(5)	118.8(5)
O(4)-S(51)-N(3)	107.5(4)
O(5)-S(51)-N(3)	114.0(4)
O(4)-S(51)-C(41)	104.4(5)
O(5)-S(51)-C(41)	104.8(4)
N(3)-S(51)-C(41)	106.2(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for import. The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12

C(1)	24(3)	23(3)	22(3)	7(2)	6(2)	6(3)
C(2)	31(4)	28(4)	35(4)	2(3)	9(3)	13(3)
C(3)	33(4)	27(4)	37(4)	3(3)	-5(3)	5(3)
C(4)	66(6)	35(4)	28(4)	0(3)	8(4)	32(4)
C(5)	51(5)	52(5)	41(4)	2(4)	8(4)	35(4)
C(6)	30(4)	28(4)	41(4)	-1(3)	11(3)	16(3)
C(7)	39(4)	18(3)	24(4)	7(3)	7(3)	14(3)
C(8)	28(4)	50(5)	46(5)	4(4)	2(4)	8(4)
C(9)	34(5)	63(6)	33(4)	21(4)	9(3)	10(4)
C(10)	43(5)	50(5)	23(4)	2(3)	3(3)	21(4)
C(11)	30(4)	40(4)	32(4)	7(3)	6(3)	8(3)
C(12)	28(4)	37(4)	32(4)	10(3)	6(3)	11(3)
C(13)	21(3)	25(3)	26(3)	9(3)	5(2)	9(2)
C(14)	23(3)	19(3)	38(4)	5(3)	6(3)	7(2)
C(15)	48(4)	37(4)	38(4)	8(3)	-6(3)	17(4)
C(16)	53(5)	38(4)	53(4)	13(3)	3(3)	21(3)
C(17)	53(4)	28(3)	46(4)	8(3)	20(3)	17(3)
C(18)	23(3)	39(4)	27(3)	-3(3)	6(2)	10(3)
C(19)	26(4)	50(5)	32(4)	10(3)	7(3)	18(3)
C(20)	32(4)	31(4)	30(4)	9(3)	16(3)	14(3)
C(21)	28(4)	23(3)	25(3)	7(3)	9(3)	12(3)
C(22)	29(4)	31(4)	37(4)	10(3)	7(3)	12(3)
C(23)	53(5)	44(5)	40(4)	3(4)	9(4)	32(4)
C(24)	72(6)	38(5)	27(4)	6(3)	5(4)	27(4)
C(25)	35(4)	27(4)	31(3)	-4(3)	-4(3)	5(3)
C(26)	32(4)	30(4)	29(4)	6(3)	6(3)	8(3)
C(27)	17(3)	33(4)	26(4)	1(3)	8(3)	15(3)
C(28)	24(4)	43(4)	32(4)	12(3)	11(3)	15(3)
C(29)	33(4)	52(5)	29(4)	9(3)	2(3)	19(4)
C(30)	38(4)	41(4)	32(4)	21(3)	16(3)	16(3)
C(31)	28(4)	49(5)	43(5)	18(4)	15(3)	15(3)

C(32)	18(3)	42(4)	30(4)	19(3)	13(3)	9(3)
C(33)	29(3)	24(3)	42(4)	8(3)	17(3)	13(3)
C(34)	24(3)	28(3)	20(3)	2(2)	9(2)	8(2)
C(35)	34(3)	32(4)	29(3)	9(3)	9(3)	13(3)
C(36)	61(5)	63(5)	51(4)	8(4)	5(4)	44(5)
C(37)	68(5)	46(4)	41(4)	1(3)	1(3)	39(4)
C(38)	24(3)	32(3)	29(3)	-1(2)	6(2)	11(2)
C(39)	33(4)	43(4)	24(3)	-5(3)	11(3)	17(3)
C(40)	19(4)	32(4)	31(4)	4(3)	5(3)	10(3)
C(41)	41(5)	42(5)	37(4)	7(3)	7(3)	15(4)
C(42)	46(5)	50(5)	33(4)	8(4)	-1(4)	23(5)
C(101)	56(6)	67(7)	59(6)	-8(5)	3(4)	31(5)
C(102)	53(5)	45(6)	67(6)	-6(5)	-11(4)	22(5)
C(103)	53(6)	34(5)	58(5)	16(4)	0(4)	5(4)
C(104)	50(5)	50(5)	48(5)	5(4)	16(4)	5(4)
C(105)	43(5)	44(5)	64(6)	1(4)	3(4)	20(4)
C(106)	44(5)	49(5)	46(4)	6(4)	-2(4)	6(4)
C(111)	49(6)	61(6)	68(6)	1(5)	10(5)	29(5)
C(112)	54(6)	83(8)	67(7)	36(6)	17(5)	33(6)
C(113)	85(10)	96(11)	33(6)	-5(6)	1(6)	38(8)
C(114)	65(7)	49(6)	106(11)	-1(7)	9(7)	25(5)
C(115)	64(7)	63(8)	121(12)	48(8)	25(7)	30(6)
C(116)	51(6)	75(7)	66(6)	20(5)	24(5)	39(5)
C(121)	78(9)	75(8)	48(7)	30(6)	19(6)	37(7)
C(122)	73(7)	65(7)	46(5)	-14(5)	-2(5)	28(6)
C(123)	48(5)	43(5)	77(7)	20(5)	19(5)	15(4)
C(124)	56(6)	64(6)	56(6)	14(5)	20(5)	14(5)
C(125)	60(6)	54(6)	64(6)	6(5)	21(5)	26(5)
C(126)	68(7)	35(5)	54(6)	9(4)	-1(5)	16(4)
C(131)	68(8)	121(12)	50(7)	-5(7)	-1(6)	47(8)
C(132)	131(12)	59(6)	38(5)	11(5)	12(6)	6(7)

C(133) 161(16) 53(7) 41(6) 3(5) -13(8) 50(10)
C(134) 78(9) 102(12) 80(10) -36(8) -11(7) 61(10)
C(135) 77(10) 132(15) 80(10) -24(10) 43(8) -11(9)
C(136) 84(8) 74(8) 36(5) 13(5) 6(5) 20(6)
C(141) 260(30) 100(13) 95(13) 58(10) 106(17) 84(18)
C(142) 220(20) 168(19) 39(7) 21(9) -6(10) 160(19)
C(143) 41(6) 178(17) 95(11) -56(11) -16(6) 48(8)
C(144) 103(10) 48(6) 71(8) -11(5) 20(7) 21(6)
C(145) 75(8) 55(6) 63(6) -1(5) 15(6) 36(6)
C(146) 127(12) 74(9) 109(12) 12(7) 84(10) 40(8)
Au(1) 23(1) 29(1) 28(1) 4(1) 7(1) 12(1)
Au(52) 20(1) 30(1) 28(1) 5(1) 7(1) 13(1)
F(1) 55(4) 40(3) 135(6) 18(3) -26(4) 0(3)
F(2) 120(5) 114(5) 102(5) 71(4) 79(4) 101(5)
F(3) 94(4) 73(4) 41(3) 18(3) 6(3) 46(4)
F(4) 100(5) 65(4) 38(3) 19(2) 14(3) 41(3)
F(5) 77(5) 54(4) 140(7) 26(4) -15(4) 5(3)
F(6) 209(10) 99(5) 67(4) 33(4) 59(5) 120(6)
N(1) 27(4) 39(4) 19(4) -2(3) 0(3) 12(3)
N(2) 29(2) 25(2) 28(2) 3(2) 6(2) 9(2)
N(3) 21(3) 42(4) 29(4) 5(3) 8(3) 23(3)
N(4) 27(2) 27(3) 27(3) 1(2) 9(2) 15(2)
O(1) 33(3) 60(4) 46(3) 3(3) -4(3) 14(3)
O(2) 41(3) 68(4) 30(3) -2(3) 9(3) 30(3)
O(3) 30(3) 55(4) 33(3) 1(3) 8(3) 20(3)
O(4) 55(4) 69(5) 27(3) -7(3) 0(3) 40(4)
O(5) 31(3) 46(3) 53(4) 3(3) -4(3) 5(2)
O(6) 27(3) 81(5) 44(4) 15(4) 12(3) 36(3)
P(1) 26(1) 22(1) 27(1) 4(1) 9(1) 12(1)
P(52) 18(1) 26(1) 22(1) 5(1) 5(1) 11(1)
S(1) 29(1) 39(1) 27(1) -2(1) -1(1) 15(1)

S(51) 28(1) 39(1) 30(1) 1(1) 1(1) 18(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for import.

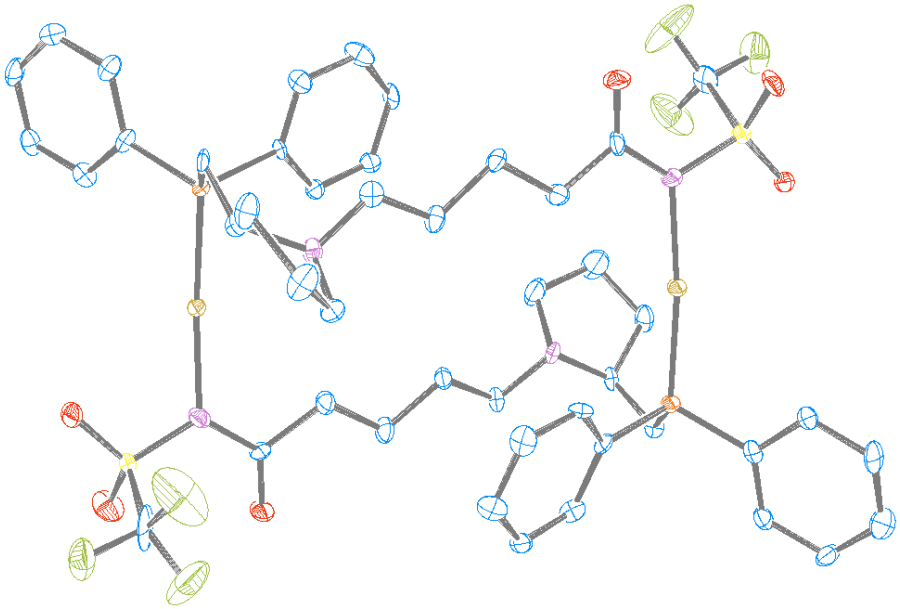
	x	y	z	U(eq)
H(2)	-1643	5413	7404	37
H(3)	-1750	3651	6602	44
H(4)	307	3437	6435	48
H(5)	2471	4929	7165	53
H(6)	2638	6704	7994	38
H(8)	-733	6530	9740	54
H(9)	9	6195	11158	54
H(10)	2376	7149	11834	46
H(11)	4005	8276	11090	43
H(12)	3311	8436	9632	40
H(14)	877	9925	8675	32
H(15A)	1255	10186	6926	51
H(15B)	-174	9899	7268	51
H(16A)	1701	12184	7150	57
H(16B)	347	11904	7572	57
H(17A)	2929	13021	8511	49
H(17B)	1626	12258	8930	49
H(18A)	4291	12188	9671	37
H(18B)	3873	10734	9541	37
H(19A)	2218	11871	10222	42
H(19B)	1846	10416	10117	42
H(22)	-2529	13603	11930	39
H(23)	-2197	15461	12765	50

H(24)	67	16830	13471	54
H(25)	1995	16387	13385	42
H(26)	1667	14522	12543	38
H(28)	-3444	11734	10313	38
H(29)	-4046	12029	8880	46
H(30)	-2290	13021	8150	42
H(31)	85	13698	8842	47
H(32)	689	13413	10272	35
H(34)	-3153	9451	12059	29
H(35A)	-209	10726	12851	38
H(35B)	-1438	9853	13282	38
H(36A)	177	9013	12546	64
H(36B)	-1349	8117	12670	64
H(37A)	-616	8619	11152	58
H(37B)	-2150	7755	11278	58
H(38A)	-3519	9690	10410	34
H(38B)	-3807	8291	10540	34
H(39A)	-1780	9658	9603	40
H(39B)	-2260	8220	9663	40
H(101)	3469	4819	966	73
H(102)	3029	5585	-341	70
H(103)	4636	5906	-1264	64
H(104)	6535	5430	-895	64
H(105)	7011	4715	379	61
H(106)	5485	4400	1319	62
H(111)	5569	5184	7267	70
H(112)	5978	5271	5878	77
H(113)	5139	3357	4927	88
H(114)	4548	1532	5513	90
H(115)	4168	1535	6896	94
H(116)	4769	3357	7790	69

H(121)	4246	6334	5005	76
H(122)	5378	8323	4679	78
H(123)	5889	8622	3329	67
H(124)	5601	6919	2342	73
H(125)	4680	4929	2698	69
H(126)	4201	4672	4059	67
H(131)	7496	2693	4373	95
H(132)	7243	1015	5061	104
H(133)	9110	554	5526	105
H(134)	11297	1709	5235	103
H(135)	11570	3435	4561	134
H(136)	9578	3853	4094	83
H(141)	9626	5989	5717	165
H(142)	12036	6999	5712	146
H(143)	12785	8767	5145	134
H(144)	11288	9637	4561	93
H(145)	8963	8684	4581	74
H(146)	8109	6881	5147	115

Table 6. Torsion angles [deg] for import.

Bidentate gold(I) complex – monomer (207)



---------- SECTION 2. COMPOUND(S) DETAILS ----------#

data_V06MB93

_audit_creation_date 2012-03-05T10:09:14-00:00
_audit_creation_method 'WinGX routine CIF_UPDATE'
_audit_conform_dict_name cif_core.dic
_audit_conform_dict_version 2.4
_audit_conform_dict_location ftp://ftp.iucr.org/pub/cif_core.dic
_publ_requested_category FM

#----------#
CHEMICAL INFORMATION
#----------#

_chemical_name_systematic
_chemical_formula_moiety 'C46 H54 Au2 F6 N4 O6 P2 S2'

```
_chemical_formula_sum                'C46 H54 Au2 F6 N4 O6 P2 S2'
_chemical_formula_weight             1392.96
_chemical_absolute_configuration     ad
_chemical_compound_source            'synthesis as described'

#------------------------------------------------------------------------------#
#                UNIT CELL INFORMATION                                         #
#------------------------------------------------------------------------------#

_symmetry_cell_setting               monoclinic
_symmetry_space_group_name_H-M       'P 21'
_symmetry_space_group_name_Hall      'P 2yb'
_symmetry_Int_Tables_number          4
loop_
   _symmetry_equiv_pos_as_xyz
'x, y, z'
'-x, y+1/2, -z'

_cell_length_a                       10.4641(2)
_cell_length_b                       17.3566(5)
_cell_length_c                       14.2244(4)
_cell_angle_alpha                    90
_cell_angle_beta                     90.8610(10)
_cell_angle_gamma                    90
_cell_volume                         2583.16(12)
_cell_formula_units_Z                2
_cell_measurement_temperature        173(2)
_cell_measurement_reflns_used        16803
#------------------------------------------------------------------------------#
#                CRYSTAL INFORMATION                                           #
#------------------------------------------------------------------------------#
```

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_exptl_crystal_description            Block
_exptl_crystal_colour                 Clear
_exptl_crystal_size_max               0.12
_exptl_crystal_size_mid               0.08
_exptl_crystal_size_min               0.06
_exptl_crystal_density_diffrn         1.791
_exptl_crystal_density_method         'not measured'
_exptl_crystal_F_000                  1360
_exptl_special_details
#---------------------------------------------------------------------------#
#                ABSORPTION CORRECTION                                      #
#---------------------------------------------------------------------------#
_exptl_absorpt_coefficient_mu         5.887
_exptl_absorpt_correction_type        multi-scan
_exptl_absorpt_process_details
;
      [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]
;
_exptl_absorpt_correction_T_min       0.5334
_exptl_absorpt_correction_T_max       0.6484
#---------------------------------------------------------------------------#
#                DATA COLLECTION                                            #
#---------------------------------------------------------------------------#
_diffrn_source                        'Enraf Nonius FR590'
_diffrn_ambient_temperature           173(2)
_diffrn_radiation_wavelength          0.71073
_diffrn_radiation_type                MoK\a
_diffrn_radiation_monochromator       graphite
_diffrn_radiation_probe               x-ray
_diffrn_detector                      'CCD plate'
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_diffrn_detector_area_resol_mean       9
_diffrn_orient_matrix_type
                        'by Bruker AXS Collect from scalepack cell'
_diffrn_orient_matrix_ub_11          -0.412969E-1
_diffrn_orient_matrix_ub_12          0.468993E-1
_diffrn_orient_matrix_ub_13          -0.277463E-1
_diffrn_orient_matrix_ub_21          -0.638734E-1
_diffrn_orient_matrix_ub_22          0
_diffrn_orient_matrix_ub_23          0.515908E-1
_diffrn_orient_matrix_ub_31          0.578745E-1
_diffrn_orient_matrix_ub_32          0.334655E-1
_diffrn_orient_matrix_ub_33          0.388843E-1
_diffrn_measurement_device           '95mm CCD camera on \k-goniostat'
_diffrn_measurement_device_type       KappaCCD
_diffrn_measurement_method           'CCD rotation images, thick slices'
_diffrn_reflns_av_R_equivalents       0.073
_diffrn_reflns_av_unetI/netI         0.0748
_diffrn_reflns_number               33846
_diffrn_reflns_limit_h_min           -13
_diffrn_reflns_limit_h_max           13
_diffrn_reflns_limit_k_min           -22
_diffrn_reflns_limit_k_max           22
_diffrn_reflns_limit_l_min           -18
_diffrn_reflns_limit_l_max           18
_diffrn_reflns_theta_min             3.44
_diffrn_reflns_theta_max             27.06
_diffrn_reflns_theta_full            27.06
_diffrn_measured_fraction_theta_full
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_diffrn_measured_fraction_theta_max
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_reflns_number_total                11184
_reflns_number_gt                   9581
_reflns_threshold_expression        >2sigma(I)

#------------------------------------------------------------------------#
#                COMPUTER PROGRAMS USED                                  #
#------------------------------------------------------------------------#

_computing_data_collection          'Collect (Bruker AXS BV, 1997-2004)'
_computing_cell_refinement
                                    'HKL Scalepack (Otwinowski & Minor 1997)'
_computing_data_reduction
                                'HKL Denzo and Scalepack (Otwinowski & Minor 1997)'
_computing_structure_solution       'SHELXS-97 (Sheldrick, 1990)'
_computing_structure_refinement     'SHELXL-97 (Sheldrick, 1997)'

#------------------------------------------------------------------------#
#                STRUCTURE SOLUTION
#------------------------------------------------------------------------#

_atom_sites_solution_primary        direct
_atom_sites_solution_secondary      difmap
_atom_sites_solution_hydrogens      geom

#------------------------------------------------------------------------#
#                REFINEMENT INFORMATION                                  #
#------------------------------------------------------------------------#

_refine_special_details
;
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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

;

_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

'calc w=1/[\s^2^(Fo^2^)+(0.0421P)^2^+11.8851P] where P=(Fo^2^+2Fc^2^)/3'

_refine_ls_hydrogen_treatment constr

_refine_ls_extinction_method none

_refine_ls_number_reflns 11184

_refine_ls_number_parameters 613

_refine_ls_number_restraints 1

_refine_ls_R_factor_all 0.0665

_refine_ls_R_factor_gt 0.0511

_refine_ls_wR_factor_ref 0.1102

_refine_ls_wR_factor_gt 0.1049

_refine_ls_goodness_of_fit_ref 1.065

_refine_ls_restrained_S_all 1.065

_refine_ls_shift/su_max 0.015

_refine_ls_shift/su_mean 0.002

_refine_ls_abs_structure_details

'Flack H D (1983), Acta Cryst. A39, 876-881'

_refine_ls_abs_structure_Flack 0.047(11)

_refine_diff_density_max 2.912

_refine_diff_density_min -1.326

_refine_diff_density_rms 0.18

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#                ATOMIC TYPES, COORDINATES AND THERMAL PARAMETERS
#
#---------------------------------------------------------------------------#

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   _atom_type_description
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   _atom_type_scat_dispersion_imag
   _atom_type_scat_source
C C 0.0033 0.0016 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
H H 0 0 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
Au Au -2.0133 8.8022 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
F F 0.0171 0.0103 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
N N 0.0061 0.0033 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
O O 0.0106 0.006 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
P P 0.1023 0.0942 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
S S 0.1246 0.1234 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

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   _atom_site_fract_x
   _atom_site_fract_y
   _atom_site_fract_z
   _atom_site_U_iso_or_equiv
   _atom_site_adp_type
   _atom_site_occupancy
   _atom_site_symmetry_multiplicity
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   _atom_site_refinement_flags
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   _atom_site_disorder_group
C1 C 0.2933(14) 0.7021(8) 0.1184(9) 0.042(4) Uani 1 1 d . . .
C2 C 0.2522(11) 0.6662(7) -0.1116(9) 0.031(3) Uani 1 1 d . . .
C3 C 0.1765(11) 0.6188(9) -0.1803(10) 0.039(3) Uani 1 1 d . . .
H3A H 0.12 0.6532 -0.2176 0.047 Uiso 1 1 calc R . .
H3B H 0.1216 0.5827 -0.1452 0.047 Uiso 1 1 calc R . .
C4 C 0.2590(11) 0.5730(7) -0.2468(9) 0.032(3) Uani 1 1 d . . .
H4A H 0.3162 0.5382 -0.2104 0.038 Uiso 1 1 calc R . .
H4B H 0.3127 0.6085 -0.2838 0.038 Uiso 1 1 calc R . .
C5 C 0.1718(11) 0.5252(7) -0.3136(8) 0.031(3) Uani 1 1 d . . .
H5A H 0.1268 0.4857 -0.2763 0.037 Uiso 1 1 calc R . .
H5B H 0.1064 0.5597 -0.3419 0.037 Uiso 1 1 calc R . .
C6 C 0.2433(11) 0.4856(7) -0.3916(8) 0.029(3) Uani 1 1 d . . .
H6A H 0.286 0.5249 -0.4305 0.035 Uiso 1 1 calc R . .
H6B H 0.3102 0.452 -0.3638 0.035 Uiso 1 1 calc R . .
C7 C 0.2231(11) 0.3827(7) -0.5128(8) 0.028(3) Uani 1 1 d . . .
H7 H 0.1533 0.3534 -0.5457 0.034 Uiso 1 1 calc R . .
C8 C 0.3027(10) 0.3239(6) -0.4612(8) 0.027(3) Uani 1 1 d . . .
H8A H 0.3769 0.3498 -0.4309 0.032 Uiso 1 1 calc R . .
H8B H 0.3356 0.2858 -0.5066 0.032 Uiso 1 1 calc R . .
C9 C 0.2877(14) 0.4319(7) -0.5883(8) 0.040(3) Uani 1 1 d . . .
H9A H 0.3031 0.4018 -0.6462 0.048 Uiso 1 1 calc R . .
H9B H 0.3695 0.4539 -0.5649 0.048 Uiso 1 1 calc R . .
C10 C 0.1860(14) 0.4954(8) -0.6052(8) 0.046(3) Uani 1 1 d . . .
H10A H 0.2265 0.5469 -0.6072 0.056 Uiso 1 1 calc R . .
H10B H 0.139 0.4866 -0.6652 0.056 Uiso 1 1 calc R . .
C11 C 0.0957(11) 0.4892(7) -0.5215(8) 0.032(3) Uani 1 1 d . . .
H11A H 0.0794 0.5408 -0.4946 0.038 Uiso 1 1 calc R . .
```

H11B H 0.0131 0.4664 -0.5417 0.038 Uiso 1 1 calc R . .

C12 C -0.2938(11) 0.8263(7) -0.1379(7) 0.024(2) Uani 1 1 d . . .

C13 C -0.2076(11) 0.8884(7) -0.1465(8) 0.027(3) Uani 1 1 d . . .

H13 H -0.1178 0.8803 -0.1469 0.033 Uiso 1 1 calc R . .

C14 C -0.2597(14) 0.9626(7) -0.1543(10) 0.040(3) Uani 1 1 d . . .

H14 H -0.2044 1.0056 -0.1603 0.048 Uiso 1 1 calc R . .

C15 C -0.3866(13) 0.9737(8) -0.1534(10) 0.044(3) Uani 1 1 d . . .

H15 H -0.4189 1.0247 -0.1585 0.052 Uiso 1 1 calc R . .

C16 C -0.4719(12) 0.9131(8) -0.1454(9) 0.037(3) Uani 1 1 d . . .

H16 H -0.5614 0.9222 -0.1452 0.045 Uiso 1 1 calc R . .

C17 C -0.4236(11) 0.8386(7) -0.1376(9) 0.031(3) Uani 1 1 d . . .

H17 H -0.4805 0.7963 -0.132 0.038 Uiso 1 1 calc R . .

C18 C -0.2575(10) 0.6843(7) -0.2367(8) 0.025(3) Uani 1 1 d . . .

C19 C -0.1600(9) 0.6791(7) -0.2987(8) 0.023(2) Uani 1 1 d . . .

H19 H -0.0788 0.6998 -0.2818 0.028 Uiso 1 1 calc R . .

C20 C -0.1765(13) 0.6437(8) -0.3875(8) 0.038(3) Uani 1 1 d . . .

H20 H -0.1069 0.6394 -0.4293 0.045 Uiso 1 1 calc R . .

C21 C -0.2967(13) 0.6152(9) -0.4125(10) 0.037(3) Uani 1 1 d . . .

H21 H -0.3086 0.5887 -0.4704 0.044 Uiso 1 1 calc R . .

C22 C -0.3986(11) 0.6254(7) -0.3532(8) 0.029(3) Uani 1 1 d . . .

H22 H -0.482 0.6109 -0.3736 0.034 Uiso 1 1 calc R . .

C23 C -0.3810(11) 0.6560(8) -0.2655(9) 0.032(3) Uani 1 1 d . . .

H23 H -0.4505 0.6586 -0.2234 0.039 Uiso 1 1 calc R . .

C51 C -0.299(2) 0.2959(7) -0.6153(12) 0.067(6) Uani 1 1 d . . .

C52 C -0.2742(9) 0.3315(8) -0.3903(9) 0.029(3) Uani 1 1 d . . .

C53 C -0.2037(11) 0.3852(8) -0.3207(10) 0.035(3) Uani 1 1 d . . .

H53A H -0.1404 0.3542 -0.2847 0.043 Uiso 1 1 calc R . .

H53B H -0.1557 0.4238 -0.3572 0.043 Uiso 1 1 calc R . .

C54 C -0.2862(12) 0.4275(8) -0.2515(9) 0.036(3) Uani 1 1 d . . .

H54A H -0.3347 0.3897 -0.2139 0.043 Uiso 1 1 calc R . .

H54B H -0.3485 0.4602 -0.2861 0.043 Uiso 1 1 calc R . .

C55 C -0.2053(10) 0.4773(7) -0.1863(9) 0.029(3) Uani 1 1 d . . .

H55A H -0.1655 0.519 -0.2233 0.034 Uiso 1 1 calc R . .

H55B H -0.1357 0.4456 -0.1585 0.034 Uiso 1 1 calc R . .

C56 C -0.2823(11) 0.5128(7) -0.1078(8) 0.030(3) Uani 1 1 d . . .

H56A H -0.3542 0.5424 -0.1357 0.036 Uiso 1 1 calc R . .

H56B H -0.3188 0.471 -0.0692 0.036 Uiso 1 1 calc R . .

C57 C -0.2805(11) 0.6150(6) 0.0149(8) 0.026(2) Uani 1 1 d . . .

H57 H -0.3534 0.5843 0.04 0.031 Uiso 1 1 calc R . .

C58 C -0.3368(10) 0.6836(7) -0.0376(8) 0.024(2) Uani 1 1 d . . .

H58A H -0.3611 0.7232 0.0089 0.029 Uiso 1 1 calc R . .

H58B H -0.4158 0.6667 -0.0707 0.029 Uiso 1 1 calc R . .

C59 C -0.1915(12) 0.6325(7) 0.0959(8) 0.039(3) Uani 1 1 d . . .

H59A H -0.1527 0.6841 0.0881 0.047 Uiso 1 1 calc R . .

H59B H -0.2382 0.6316 0.1558 0.047 Uiso 1 1 calc R . .

C60 C -0.0905(16) 0.5715(9) 0.0957(10) 0.067(5) Uani 1 1 d . . .

H60A H -0.0047 0.5949 0.0899 0.081 Uiso 1 1 calc R . .

H60B H -0.0925 0.5411 0.1545 0.081 Uiso 1 1 calc R . .

C61 C -0.1194(14) 0.5224(9) 0.0145(11) 0.052(4) Uani 1 1 d . . .

H61A H -0.0398 0.5099 -0.019 0.062 Uiso 1 1 calc R . .

H61B H -0.1589 0.4736 0.0354 0.062 Uiso 1 1 calc R . .

C62 C 0.2447(9) 0.3211(6) -0.2586(7) 0.019(2) Uani 1 1 d . . .

C63 C 0.1457(10) 0.3337(7) -0.1967(8) 0.026(3) Uani 1 1 d . . .

H63 H 0.0614 0.3178 -0.213 0.031 Uiso 1 1 calc R . .

C64 C 0.1693(10) 0.3690(7) -0.1121(9) 0.031(3) Uani 1 1 d . . .

H64 H 0.1019 0.3785 -0.0696 0.038 Uiso 1 1 calc R . .

C65 C 0.2924(12) 0.3905(7) -0.0898(8) 0.030(3) Uani 1 1 d . . .

H65 H 0.3087 0.4154 -0.0314 0.037 Uiso 1 1 calc R . .

C66 C 0.3905(12) 0.3775(8) -0.1471(9) 0.040(3) Uani 1 1 d . . .

H66 H 0.4748 0.3931 -0.1301 0.047 Uiso 1 1 calc R . .

C67 C 0.3649(11) 0.3402(8) -0.2333(9) 0.031(3) Uani 1 1 d . . .

H67 H 0.4334 0.3284 -0.2739 0.038 Uiso 1 1 calc R . .

C68 C 0.2787(11) 0.1791(7) -0.3606(8) 0.027(3) Uani 1 1 d . . .

C69 C 0.1997(12) 0.1159(7) -0.3489(8) 0.030(3) Uani 1 1 d . . .

H69 H 0.1099 0.1236 -0.3479 0.036 Uiso 1 1 calc R . .

C70 C 0.2467(12) 0.0431(7) -0.3386(9) 0.033(3) Uani 1 1 d . . .

H70 H 0.19 0.0007 -0.3325 0.04 Uiso 1 1 calc R . .

C71 C 0.3781(13) 0.0313(8) -0.3372(10) 0.039(3) Uani 1 1 d . . .

H71 H 0.4114 -0.0192 -0.3287 0.047 Uiso 1 1 calc R . .

C72 C 0.4599(12) 0.0924(8) -0.3480(10) 0.043(4) Uani 1 1 d . . .

H72 H 0.5497 0.0843 -0.3489 0.052 Uiso 1 1 calc R . .

C73 C 0.4104(11) 0.1659(8) -0.3576(9) 0.034(3) Uani 1 1 d . . .

H73 H 0.4672 0.2083 -0.3622 0.041 Uiso 1 1 calc R . .

Au1 Au -0.02337(3) 0.72464(2) -0.08346(3) 0.02374(11) Uani 1 1 d . . .

Au51 Au 0.00247(3) 0.275212(18) -0.40897(3) 0.02232(11) Uani 1 1 d . . .

F1 F 0.3238(11) 0.7405(6) 0.1930(6) 0.082(3) Uani 1 1 d . . .

F2 F 0.2091(14) 0.6553(8) 0.1420(10) 0.121(5) Uani 1 1 d . . .

F3 F 0.3948(14) 0.6666(8) 0.0926(8) 0.123(6) Uani 1 1 d . . .

F51 F -0.2148(17) 0.3508(8) -0.6327(10) 0.146(7) Uani 1 1 d . . .

F52 F -0.3188(10) 0.2592(6) -0.6954(6) 0.073(3) Uani 1 1 d . . .

F53 F -0.4058(14) 0.3325(9) -0.5980(8) 0.126(6) Uani 1 1 d . . .

N1 N 0.1722(8) 0.7114(7) -0.0552(7) 0.031(3) Uani 1 1 d . . .

N2 N 0.1589(9) 0.4396(5) -0.4512(6) 0.028(2) Uani 1 1 d . . .

N51 N -0.1909(9) 0.2843(8) -0.4420(7) 0.030(2) Uani 1 1 d . . .

N52 N -0.2064(8) 0.5637(5) -0.0471(7) 0.026(2) Uani 1 1 d . . .

O1 O 0.1290(7) 0.8072(5) 0.0692(6) 0.037(2) Uani 1 1 d . . .

O2 O 0.3430(8) 0.8109(5) -0.0021(6) 0.038(2) Uani 1 1 d . . .

O3 O 0.3655(7) 0.6645(6) -0.1040(7) 0.049(3) Uani 1 1 d . . .

O51 O -0.1413(8) 0.1896(6) -0.5638(6) 0.045(3) Uani 1 1 d . . .

O52 O -0.3574(9) 0.1877(6) -0.5005(7) 0.055(3) Uani 1 1 d . . .

O53 O -0.3886(7) 0.3325(6) -0.3993(6) 0.043(2) Uani 1 1 d . . .

P1 P -0.2310(2) 0.7280(3) -0.1233(2) 0.0233(6) Uani 1 1 d . . .

P51 P 0.2104(2) 0.2739(2) -0.37149(18) 0.0197(5) Uani 1 1 d . . .

S5 S -0.2470(2) 0.2316(2) -0.52353(19) 0.0255(6) Uani 1 1 d . . .
S6 S 0.2324(2) 0.7691(2) 0.0254(2) 0.0290(6) Uani 1 1 d . . .

loop_
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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_23
_atom_site_aniso_U_13
_atom_site_aniso_U_12
C1 0.059(8) 0.047(11) 0.019(7) -0.006(6) -0.013(6) 0.001(7)
C2 0.035(6) 0.016(6) 0.041(8) -0.008(5) 0.005(5) -0.007(5)
C3 0.024(6) 0.053(9) 0.040(8) -0.025(7) 0.001(5) 0.006(6)
C4 0.030(6) 0.031(7) 0.033(7) -0.010(6) 0.004(5) 0.011(5)
C5 0.036(6) 0.023(6) 0.034(7) -0.002(5) 0.014(5) -0.001(5)
C6 0.039(7) 0.027(7) 0.022(6) 0.007(5) 0.002(5) 0.000(5)
C7 0.032(6) 0.036(7) 0.017(6) -0.003(5) 0.002(5) 0.006(5)
C8 0.032(6) 0.012(5) 0.038(7) -0.011(5) 0.007(5) 0.000(4)
C9 0.063(9) 0.032(7) 0.026(6) 0.000(5) 0.012(6) 0.007(6)
C10 0.070(9) 0.050(8) 0.019(6) 0.007(5) 0.009(6) 0.021(7)
C11 0.036(6) 0.024(6) 0.035(7) 0.005(5) -0.008(5) 0.006(5)
C12 0.036(6) 0.024(6) 0.013(6) -0.001(5) -0.001(5) -0.005(5)
C13 0.034(6) 0.031(7) 0.017(6) -0.010(5) -0.001(5) 0.002(5)
C14 0.064(9) 0.015(7) 0.040(8) 0.008(6) 0.003(7) -0.008(6)
C15 0.054(9) 0.034(8) 0.042(9) 0.008(6) 0.009(7) 0.001(6)
C16 0.037(7) 0.033(8) 0.041(8) 0.002(6) -0.007(6) 0.015(5)
C17 0.030(6) 0.025(7) 0.039(8) -0.005(6) 0.000(5) -0.007(5)
C18 0.020(5) 0.024(6) 0.031(7) -0.005(5) 0.006(5) 0.009(4)
C19 0.013(5) 0.033(6) 0.023(6) 0.006(5) -0.002(4) -0.004(4)
C20 0.056(8) 0.041(8) 0.016(6) 0.003(5) 0.005(6) 0.003(6)

C21 0.041(7) 0.049(9) 0.021(7) 0.012(6) -0.004(6) -0.005(6)

C22 0.026(6) 0.036(7) 0.023(7) -0.006(5) -0.002(5) 0.006(5)

C23 0.030(6) 0.039(8) 0.029(7) 0.007(6) 0.006(5) 0.006(5)

C51 0.138(16) 0.006(8) 0.058(11) -0.006(6) 0.002(11) 0.008(8)

C52 0.011(5) 0.040(8) 0.036(7) -0.011(6) 0.006(5) 0.004(5)

C53 0.027(6) 0.037(8) 0.043(8) -0.017(6) 0.007(6) -0.001(5)

C54 0.041(7) 0.033(7) 0.034(7) -0.012(6) 0.008(6) 0.002(5)

C55 0.026(6) 0.024(6) 0.037(7) -0.010(5) 0.004(5) -0.004(4)

C56 0.041(7) 0.019(6) 0.030(6) -0.006(5) 0.004(5) -0.005(5)

C57 0.036(6) 0.019(5) 0.023(6) -0.007(4) 0.004(5) -0.003(5)

C58 0.029(6) 0.025(6) 0.019(6) 0.001(5) 0.005(4) 0.000(5)

C59 0.062(8) 0.029(6) 0.026(6) -0.005(5) -0.002(6) 0.002(6)

C60 0.084(12) 0.071(10) 0.047(9) -0.015(8) -0.022(8) 0.032(9)

C61 0.066(9) 0.037(8) 0.053(9) -0.007(7) -0.011(7) 0.023(7)

C62 0.025(5) 0.018(6) 0.014(5) -0.006(4) -0.001(4) -0.003(4)

C63 0.028(6) 0.029(6) 0.021(6) -0.005(5) -0.003(5) 0.003(5)

C64 0.024(6) 0.034(7) 0.036(7) -0.007(5) 0.003(5) -0.001(5)

C65 0.048(7) 0.031(7) 0.012(6) -0.012(5) -0.003(5) 0.003(5)

C66 0.039(7) 0.057(9) 0.022(7) 0.005(6) -0.006(6) -0.014(6)

C67 0.033(6) 0.039(8) 0.023(7) -0.002(6) 0.002(5) -0.005(5)

C68 0.032(6) 0.023(6) 0.026(7) 0.001(5) 0.005(5) 0.010(5)

C69 0.035(6) 0.031(7) 0.024(7) 0.005(5) 0.003(5) -0.007(5)

C70 0.050(8) 0.025(7) 0.024(7) 0.000(5) -0.005(6) -0.004(5)

C71 0.055(8) 0.022(7) 0.042(8) -0.004(6) -0.003(6) 0.015(6)

C72 0.029(6) 0.044(9) 0.057(10) -0.007(7) -0.004(6) 0.005(6)

C73 0.039(7) 0.031(8) 0.033(7) 0.002(6) 0.003(6) 0.012(6)

Au1 0.01868(17) 0.0267(3) 0.0259(2) -0.0052(2) 0.00168(16) -0.00040(18)

Au51 0.01865(17) 0.0228(2) 0.0256(2) -0.00450(19) 0.00172(15) 0.00006(17)

F1 0.139(9) 0.064(9) 0.042(5) -0.006(5) -0.031(6) 0.009(6)

F2 0.144(11) 0.095(10) 0.122(11) 0.045(9) -0.058(9) -0.067(9)

F3 0.164(12) 0.140(11) 0.064(7) 0.036(8) 0.019(8) 0.119(10)

F51 0.238(17) 0.082(10) 0.115(11) 0.067(9) -0.065(11) -0.087(10)
F52 0.124(8) 0.051(8) 0.044(5) -0.012(5) -0.009(5) 0.020(5)
F53 0.173(13) 0.143(12) 0.061(7) -0.007(8) -0.011(8) 0.120(11)
N1 0.020(4) 0.036(8) 0.037(6) -0.012(5) 0.000(4) 0.005(4)
N2 0.035(5) 0.028(5) 0.021(5) -0.007(4) 0.006(4) 0.000(4)
N51 0.029(5) 0.025(6) 0.036(6) 0.000(5) -0.008(4) -0.006(5)
N52 0.033(5) 0.016(5) 0.028(5) -0.003(4) 0.003(4) 0.007(4)
O1 0.031(4) 0.037(5) 0.042(5) -0.023(4) -0.009(4) 0.008(3)
O2 0.035(4) 0.032(5) 0.047(6) -0.008(4) 0.002(4) -0.018(4)
O3 0.022(4) 0.068(7) 0.056(6) -0.032(5) -0.004(4) 0.012(4)
O51 0.030(4) 0.058(7) 0.046(6) -0.030(5) 0.004(4) 0.005(4)
O52 0.042(5) 0.072(8) 0.052(7) -0.008(5) 0.011(5) -0.023(5)
O53 0.017(4) 0.057(6) 0.055(6) -0.025(5) 0.002(4) -0.001(4)
P1 0.0170(12) 0.0262(16) 0.0269(15) -0.0046(16) 0.0013(10) 0.0013(15)
P51 0.0166(11) 0.0208(14) 0.0218(13) -0.0037(16) 0.0002(10) 0.0020(15)
S5 0.0251(12) 0.0221(16) 0.0294(15) -0.0074(14) -0.0032(11) -0.0003(12)
S6 0.0239(12) 0.0288(17) 0.0343(16) -0.0098(16) -0.0018(11) 0.0004(14)

#---#
MOLECULAR GEOMETRY
#---#

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.

;

loop_

_geom_bond_atom_site_label_1

_geom_bond_atom_site_label_2

_geom_bond_distance

_geom_bond_site_symmetry_2

_geom_bond_publ_flag

C1 F2 1.249(17) . ?

C1 F3 1.285(16) . ?

C1 F1 1.289(16) . ?

C1 S6 1.866(14) . ?

C2 O3 1.189(13) . ?

C2 N1 1.407(15) . ?

C2 C3 1.496(18) . ?

C3 C4 1.515(15) . ?

C3 H3A 0.99 . ?

C3 H3B 0.99 . ?

C4 C5 1.549(18) . ?

C4 H4A 0.99 . ?

C4 H4B 0.99 . ?

C5 C6 1.513(15) . ?

C5 H5A 0.99 . ?

C5 H5B 0.99 . ?

C6 N2 1.453(15) . ?

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C6 H6B 0.99 . ?

C7 N2 1.487(14) . ?

C7 C8 1.501(16) . ?

C7 C9 1.537(16) . ?

C7 H7 1 . ?

C8 P51 1.830(11) . ?

C8 H8A 0.99 . ?
C8 H8B 0.99 . ?
C9 C10 1.548(17) . ?
C9 H9A 0.99 . ?
C9 H9B 0.99 . ?
C10 C11 1.535(16) . ?
C10 H10A 0.99 . ?
C10 H10B 0.99 . ?
C11 N2 1.469(14) . ?
C11 H11A 0.99 . ?
C11 H11B 0.99 . ?
C12 C17 1.376(16) . ?
C12 C13 1.413(16) . ?
C12 P1 1.838(13) . ?
C13 C14 1.402(18) . ?
C13 H13 0.95 . ?
C14 C15 1.342(19) . ?
C14 H14 0.95 . ?
C15 C16 1.384(19) . ?
C15 H15 0.95 . ?
C16 C17 1.392(18) . ?
C16 H16 0.95 . ?
C17 H17 0.95 . ?
C18 C19 1.362(13) . ?
C18 C23 1.436(17) . ?
C18 P1 1.801(12) . ?
C19 C20 1.412(17) . ?
C19 H19 0.95 . ?
C20 C21 1.393(19) . ?
C20 H20 0.95 . ?
C21 C22 1.382(16) . ?

C21 H21 0.95 . ?
C22 C23 1.366(17) . ?
C22 H22 0.95 . ?
C23 H23 0.95 . ?
C51 F53 1.31(2) . ?
C51 F51 1.32(2) . ?
C51 F52 1.319(18) . ?
C51 S5 1.797(17) . ?
C52 O53 1.203(12) . ?
C52 N51 1.411(15) . ?
C52 C53 1.540(18) . ?
C53 C54 1.509(16) . ?
C53 H53A 0.99 . ?
C53 H53B 0.99 . ?
C54 C55 1.517(17) . ?
C54 H54A 0.99 . ?
C54 H54B 0.99 . ?
C55 C56 1.517(15) . ?
C55 H55A 0.99 . ?
C55 H55B 0.99 . ?
C56 N52 1.462(15) . ?
C56 H56A 0.99 . ?
C56 H56B 0.99 . ?
C57 N52 1.481(13) . ?
C57 C59 1.501(16) . ?
C57 C58 1.519(16) . ?
C57 H57 1 . ?
C58 P1 1.830(10) . ?
C58 H58A 0.99 . ?
C58 H58B 0.99 . ?
C59 C60 1.496(18) . ?

C59 H59A 0.99 . ?
C59 H59B 0.99 . ?
C60 C61 1.46(2) . ?
C60 H60A 0.99 . ?
C60 H60B 0.99 . ?
C61 N52 1.445(16) . ?
C61 H61A 0.99 . ?
C61 H61B 0.99 . ?
C62 C67 1.345(15) . ?
C62 C63 1.387(13) . ?
C62 P51 1.833(11) . ?
C63 C64 1.370(16) . ?
C63 H63 0.95 . ?
C64 C65 1.373(17) . ?
C64 H64 0.95 . ?
C65 C66 1.339(16) . ?
C65 H65 0.95 . ?
C66 C67 1.409(18) . ?
C66 H66 0.95 . ?
C67 H67 0.95 . ?
C68 C69 1.385(17) . ?
C68 C73 1.397(15) . ?
C68 P51 1.800(12) . ?
C69 C70 1.363(18) . ?
C69 H69 0.95 . ?
C70 C71 1.390(18) . ?
C70 H70 0.95 . ?
C71 C72 1.373(19) . ?
C71 H71 0.95 . ?
C72 C73 1.382(19) . ?
C72 H72 0.95 . ?

C73 H73 0.95 . ?

Au1 N1 2.093(9) . ?

Au1 P1 2.238(3) . ?

Au51 N51 2.076(9) . ?

Au51 P51 2.232(2) . ?

N1 S6 1.640(11) . ?

N51 S5 1.583(12) . ?

O1 S6 1.421(8) . ?

O2 S6 1.425(8) . ?

O51 S5 1.450(8) . ?

O52 S5 1.426(9) . ?

loop_

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_geom_angle_atom_site_label_3

_geom_angle

_geom_angle_site_symmetry_1

_geom_angle_site_symmetry_3

_geom_angle_publ_flag

F2 C1 F3 110.7(16) . . ?

F2 C1 F1 106.4(13) . . ?

F3 C1 F1 106.7(13) . . ?

F2 C1 S6 111.2(11) . . ?

F3 C1 S6 111.8(10) . . ?

F1 C1 S6 109.8(10) . . ?

O3 C2 N1 124.2(12) . . ?

O3 C2 C3 124.3(11) . . ?

N1 C2 C3 111.5(10) . . ?

C2 C3 C4 113.3(10) . . ?

C2 C3 H3A 108.9 . . ?

C4 C3 H3A 108.9 . . ?

C2 C3 H3B 108.9 . . ?

C4 C3 H3B 108.9 . . ?

H3A C3 H3B 107.7 . . ?

C3 C4 C5 109.1(10) . . ?

C3 C4 H4A 109.9 . . ?

C5 C4 H4A 109.9 . . ?

C3 C4 H4B 109.9 . . ?

C5 C4 H4B 109.9 . . ?

H4A C4 H4B 108.3 . . ?

C6 C5 C4 113.6(9) . . ?

C6 C5 H5A 108.8 . . ?

C4 C5 H5A 108.8 . . ?

C6 C5 H5B 108.8 . . ?

C4 C5 H5B 108.8 . . ?

H5A C5 H5B 107.7 . . ?

N2 C6 C5 112.0(10) . . ?

N2 C6 H6A 109.2 . . ?

C5 C6 H6A 109.2 . . ?

N2 C6 H6B 109.2 . . ?

C5 C6 H6B 109.2 . . ?

H6A C6 H6B 107.9 . . ?

N2 C7 C8 114.5(9) . . ?

N2 C7 C9 104.5(9) . . ?

C8 C7 C9 118.2(9) . . ?

N2 C7 H7 106.3 . . ?

C8 C7 H7 106.3 . . ?

C9 C7 H7 106.3 . . ?

C7 C8 P51 111.6(7) . . ?

C7 C8 H8A 109.3 . . ?

P51 C8 H8A 109.3 . . ?

C7 C8 H8B 109.3 . . ?
P51 C8 H8B 109.3 . . ?
H8A C8 H8B 108 . . ?
C7 C9 C10 101.3(10) . . ?
C7 C9 H9A 111.5 . . ?
C10 C9 H9A 111.5 . . ?
C7 C9 H9B 111.5 . . ?
C10 C9 H9B 111.5 . . ?
H9A C9 H9B 109.3 . . ?
C11 C10 C9 105.0(9) . . ?
C11 C10 H10A 110.8 . . ?
C9 C10 H10A 110.8 . . ?
C11 C10 H10B 110.8 . . ?
C9 C10 H10B 110.8 . . ?
H10A C10 H10B 108.8 . . ?
N2 C11 C10 107.1(9) . . ?
N2 C11 H11A 110.3 . . ?
C10 C11 H11A 110.3 . . ?
N2 C11 H11B 110.3 . . ?
C10 C11 H11B 110.3 . . ?
H11A C11 H11B 108.6 . . ?
C17 C12 C13 120.9(11) . . ?
C17 C12 P1 119.7(9) . . ?
C13 C12 P1 119.4(9) . . ?
C14 C13 C12 117.4(11) . . ?
C14 C13 H13 121.3 . . ?
C12 C13 H13 121.3 . . ?
C15 C14 C13 121.0(12) . . ?
C15 C14 H14 119.5 . . ?
C13 C14 H14 119.5 . . ?
C14 C15 C16 122.1(13) . . ?

C14 C15 H15 119 . . ?
C16 C15 H15 119 . . ?
C15 C16 C17 118.6(11) . . ?
C15 C16 H16 120.7 . . ?
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C12 C17 C16 120.1(11) . . ?
C12 C17 H17 119.9 . . ?
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C19 C18 C23 118.2(11) . . ?
C19 C18 P1 120.1(9) . . ?
C23 C18 P1 121.7(8) . . ?
C18 C19 C20 121.6(10) . . ?
C18 C19 H19 119.2 . . ?
C20 C19 H19 119.2 . . ?
C21 C20 C19 118.8(11) . . ?
C21 C20 H20 120.6 . . ?
C19 C20 H20 120.6 . . ?
C22 C21 C20 120.0(13) . . ?
C22 C21 H21 120 . . ?
C20 C21 H21 120 . . ?
C23 C22 C21 120.9(12) . . ?
C23 C22 H22 119.6 . . ?
C21 C22 H22 119.5 . . ?
C22 C23 C18 120.1(10) . . ?
C22 C23 H23 119.9 . . ?
C18 C23 H23 119.9 . . ?
F53 C51 F51 105.0(15) . . ?
F53 C51 F52 105.9(16) . . ?
F51 C51 F52 106.4(15) . . ?
F53 C51 S5 114.5(12) . . ?
F51 C51 S5 112.7(15) . . ?

F52 C51 S5 111.7(9) . . ?

O53 C52 N51 125.1(12) . . ?

O53 C52 C53 121.7(10) . . ?

N51 C52 C53 113.1(9) . . ?

C54 C53 C52 116.1(10) . . ?

C54 C53 H53A 108.3 . . ?

C52 C53 H53A 108.3 . . ?

C54 C53 H53B 108.3 . . ?

C52 C53 H53B 108.3 . . ?

H53A C53 H53B 107.4 . . ?

C53 C54 C55 110.8(10) . . ?

C53 C54 H54A 109.5 . . ?

(*S*)-4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-4-oxobutanoic acid

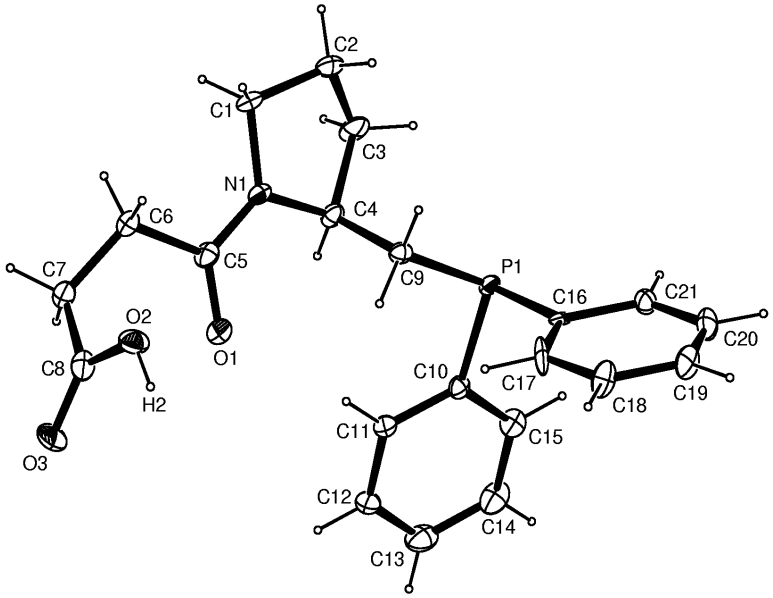

Table 1. Crystal data and structure refinement for may410 *** **data low quality and not publishable** ***

Identification code	may410	
Empirical formula	C23 H24 N O3 P, 0.5 C6 H6	
Formula weight	408.44	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* 1 (No.1)	
Unit cell dimensions	a = 7.8376(3) Å	a= 101.276(2)°.
	b = 9.0195(3) Å	b= 93.631(2)°.
	c = 17.5032(6) Å	g = 115.456(2)°.
Volume	1080.35(7) $Å^3$	
Z	2	
Density (calculated)	1.26 Mg/m^3	
Absorption coefficient	0.15 mm^{-1}	
F(000)	434	
Crystal size	0.16 x 0.15 x 0.05 mm^3	

Theta range for data collection	3.46 to 26.70°.
Index ranges	-9<=h<=9, -11<=k<=11, -22<=l<=22
Reflections collected	17876
Independent reflections	4550 [R(int) = 0.081]
Reflections with I>2sigma(I)	4323
Completeness to theta = 26.70°	99.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4550 / 111 / 496
Goodness-of-fit on F^2	1.014
Final R indices [I>2sigma(I)]	R1 = 0.097, wR2 = 0.259
R indices (all data)	R1 = 0.101, wR2 = 0.263
Absolute structure parameter	0.2(2)
Largest diff. peak and hole	1.931 and -0.522 e.Å^{-3}

The plate-like crystals were of low quality and while sufficient data was collected to identify and solve the structure (in space group *P*1), the quality of the data is insufficient for publication.

Data collection KappaCCD , Program package WinGX , Abs correction not applied
Refinement using SHELXL-97 , Drawing using ORTEP-3 for Windows

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for may410. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	8155(2)	5155(2)	4763(1)	20(1)
P(2)	1929(2)	3592(2)	1094(1)	20(1)
O(1)	8384(9)	4224(7)	7272(4)	33(1)

O(2)	4826(9)	2684(8)	8248(4)	35(1)
O(3)	7142(11)	4470(8)	9272(4)	42(2)
O(4)	3033(10)	4651(7)	-1365(3)	33(1)
O(5)	6469(10)	6135(9)	-2337(4)	37(1)
O(6)	4125(12)	4410(9)	-3343(4)	45(2)
N(1)	7820(10)	2019(8)	6251(4)	24(1)
N(2)	4442(10)	6875(8)	-300(4)	24(1)
C(1)	7151(15)	203(10)	5897(5)	34(2)
C(2)	7242(16)	156(11)	5030(5)	38(2)
C(3)	8857(15)	1871(11)	5030(6)	35(2)
C(4)	8597(11)	3097(10)	5694(5)	24(2)
C(5)	7866(11)	2704(10)	7011(5)	26(2)
C(6)	7217(13)	1471(11)	7545(5)	29(2)
C(7)	7686(14)	2382(11)	8413(5)	33(2)
C(8)	6552(12)	3304(11)	8685(5)	31(2)
C(9)	7189(11)	3716(9)	5419(4)	22(1)
C(10)	9763(11)	7201(9)	5443(4)	22(1)
C(11)	10088(13)	7470(10)	6261(5)	28(2)
C(12)	11392(15)	9086(11)	6726(5)	37(2)
C(13)	12382(15)	10397(12)	6392(7)	45(2)
C(14)	12071(13)	10106(12)	5566(7)	39(2)
C(15)	10788(11)	8522(11)	5101(5)	29(2)
C(16)	6061(10)	5485(9)	4501(5)	24(2)
C(17)	4860(13)	5565(12)	4958(5)	36(2)
C(18)	3270(12)	5802(13)	4687(6)	34(2)
C(19)	2995(12)	5982(12)	3925(5)	34(2)
C(20)	4284(13)	5935(12)	3444(5)	34(2)
C(21)	5803(12)	5674(10)	3716(5)	26(2)
C(22)	5548(14)	8687(10)	81(5)	33(2)
C(23)	5846(14)	8700(11)	960(5)	42(2)
C(24)	5810(11)	7039(11)	959(5)	32(2)

C(25)	4263(10)	5796(9)	258(4)	21(1)
C(26)	3871(12)	6202(10)	-1083(5)	26(2)
C(27)	4261(14)	7444(10)	-1600(5)	31(2)
C(28)	3675(15)	6523(12)	-2463(5)	34(2)
C(29)	4698(14)	5531(10)	-2765(5)	32(2)
C(30)	2233(10)	5080(9)	464(4)	19(1)
C(31)	1263(10)	1573(9)	385(5)	22(2)
C(32)	1085(14)	1319(11)	-423(5)	34(2)
C(33)	539(17)	-257(13)	-919(7)	49(3)
C(34)	249(16)	-1627(12)	-608(8)	48(3)
C(35)	459(14)	-1408(11)	207(7)	41(2)
C(36)	974(12)	169(10)	702(6)	32(2)
C(37)	-418(10)	3288(8)	1358(4)	21(1)
C(38)	-1843(12)	3255(10)	883(5)	29(2)
C(39)	-3591(12)	3020(11)	1131(6)	30(2)
C(40)	-3828(13)	2882(12)	1915(6)	36(2)
C(41)	-2345(12)	2948(11)	2396(5)	30(2)
C(42)	-643(11)	3146(9)	2145(4)	22(1)
C(43)	-191(12)	8031(15)	2558(7)	50(5)
C(44)	1557(19)	7993(10)	2524(6)	32(3)
C(45)	3246(12)	9403(15)	2911(7)	39(4)
C(46)	3188(15)	10851(10)	3333(6)	27(3)
C(47)	1440(20)	10890(14)	3367(6)	36(4)
C(48)	-250(14)	9480(20)	2980(8)	49(5)
C(43A)	320(50)	7770(20)	2471(14)	49(8)
C(44A)	2310(50)	8490(50)	2660(20)	87(15)
C(45A)	3330(20)	10140(50)	3120(20)	120(20)
C(46A)	2370(40)	11070(30)	3392(15)	56(9)
C(47A)	390(40)	10360(30)	3204(13)	38(7)
C(48A)	-640(20)	8710(30)	2744(14)	39(7)

Table 3. Bond lengths [Å] and angles [°] for may410.

P(1)-C(10)	1.835(8)
P(1)-C(16)	1.836(7)
P(1)-C(9)	1.851(8)
P(2)-C(31)	1.830(8)
P(2)-C(37)	1.843(7)
P(2)-C(30)	1.847(7)
O(1)-C(5)	1.227(10)
O(2)-C(8)	1.333(11)
O(3)-C(8)	1.214(11)
O(4)-C(26)	1.238(10)
O(5)-C(29)	1.358(12)
O(6)-C(29)	1.183(11)
N(1)-C(5)	1.344(11)
N(1)-C(1)	1.471(10)
N(1)-C(4)	1.484(10)
N(2)-C(26)	1.345(10)
N(2)-C(22)	1.466(10)
N(2)-C(25)	1.480(9)
C(1)-C(2)	1.517(13)
C(2)-C(3)	1.520(14)
C(3)-C(4)	1.528(11)
C(4)-C(9)	1.526(10)
C(5)-C(6)	1.532(11)
C(6)-C(7)	1.518(12)
C(7)-C(8)	1.498(13)
C(10)-C(11)	1.392(11)
C(10)-C(15)	1.394(11)
C(11)-C(12)	1.407(11)
C(12)-C(13)	1.371(15)

C(13)-C(14)	1.405(16)
C(14)-C(15)	1.386(13)
C(16)-C(17)	1.288(13)
C(16)-C(21)	1.430(11)
C(17)-C(18)	1.420(12)
C(18)-C(19)	1.390(13)
C(19)-C(20)	1.364(14)
C(20)-C(21)	1.382(12)
C(22)-C(23)	1.539(12)
C(23)-C(24)	1.486(15)
C(24)-C(25)	1.529(10)
C(25)-C(30)	1.536(9)
C(26)-C(27)	1.519(10)
C(27)-C(28)	1.507(12)
C(28)-C(29)	1.487(13)
C(31)-C(32)	1.375(12)
C(31)-C(36)	1.416(10)
C(32)-C(33)	1.380(13)
C(33)-C(34)	1.382(16)
C(34)-C(35)	1.391(17)
C(35)-C(36)	1.384(13)
C(37)-C(38)	1.335(12)
C(37)-C(42)	1.423(10)
C(38)-C(39)	1.404(12)
C(39)-C(40)	1.419(13)
C(40)-C(41)	1.365(14)
C(41)-C(42)	1.380(11)

C(10)-P(1)-C(16)	101.4(3)
C(10)-P(1)-C(9)	104.0(3)
C(16)-P(1)-C(9)	99.7(4)

C(31)-P(2)-C(37)	101.1(3)
C(31)-P(2)-C(30)	103.6(3)
C(37)-P(2)-C(30)	99.2(3)
C(5)-N(1)-C(1)	125.3(7)
C(5)-N(1)-C(4)	121.3(6)
C(1)-N(1)-C(4)	113.3(6)
C(26)-N(2)-C(22)	125.3(7)
C(26)-N(2)-C(25)	121.4(6)
C(22)-N(2)-C(25)	112.6(6)
N(1)-C(1)-C(2)	102.3(7)
C(1)-C(2)-C(3)	104.6(8)
C(2)-C(3)-C(4)	103.5(7)
N(1)-C(4)-C(9)	110.8(6)
N(1)-C(4)-C(3)	101.5(6)
C(9)-C(4)-C(3)	113.0(7)
O(1)-C(5)-N(1)	122.8(7)
O(1)-C(5)-C(6)	121.0(7)
N(1)-C(5)-C(6)	116.1(7)
C(7)-C(6)-C(5)	112.3(7)
C(8)-C(7)-C(6)	116.5(7)
O(3)-C(8)-O(2)	123.6(9)
O(3)-C(8)-C(7)	122.2(8)
O(2)-C(8)-C(7)	114.1(8)
C(4)-C(9)-P(1)	112.2(5)
C(11)-C(10)-C(15)	119.3(7)
C(11)-C(10)-P(1)	124.2(6)
C(15)-C(10)-P(1)	116.5(6)
C(10)-C(11)-C(12)	119.3(8)
C(13)-C(12)-C(11)	121.7(9)
C(12)-C(13)-C(14)	118.6(8)
C(15)-C(14)-C(13)	120.3(9)

C(14)-C(15)-C(10)	120.8(8)
C(17)-C(16)-C(21)	119.2(7)
C(17)-C(16)-P(1)	125.9(6)
C(21)-C(16)-P(1)	114.9(6)
C(16)-C(17)-C(18)	121.0(7)
C(19)-C(18)-C(17)	120.5(8)
C(20)-C(19)-C(18)	118.8(8)
C(19)-C(20)-C(21)	119.6(8)
C(20)-C(21)-C(16)	120.8(7)
N(2)-C(22)-C(23)	102.5(7)
C(24)-C(23)-C(22)	104.7(7)
C(23)-C(24)-C(25)	104.2(7)
N(2)-C(25)-C(24)	102.0(6)
N(2)-C(25)-C(30)	110.4(6)
C(24)-C(25)-C(30)	113.4(6)
O(4)-C(26)-N(2)	121.8(7)
O(4)-C(26)-C(27)	121.7(7)
N(2)-C(26)-C(27)	116.6(7)
C(28)-C(27)-C(26)	110.8(7)
C(29)-C(28)-C(27)	116.4(8)
O(6)-C(29)-O(5)	122.3(9)
O(6)-C(29)-C(28)	125.1(10)
O(5)-C(29)-C(28)	112.4(7)
C(25)-C(30)-P(2)	110.9(5)
C(32)-C(31)-C(36)	117.6(8)
C(32)-C(31)-P(2)	125.7(6)
C(36)-C(31)-P(2)	116.7(7)
C(31)-C(32)-C(33)	122.0(9)
C(32)-C(33)-C(34)	120.2(11)
C(33)-C(34)-C(35)	119.3(9)
C(36)-C(35)-C(34)	120.3(8)

C(35)-C(36)-C(31)	120.5(9)
C(38)-C(37)-C(42)	119.4(7)
C(38)-C(37)-P(2)	125.2(6)
C(42)-C(37)-P(2)	115.4(6)
C(37)-C(38)-C(39)	121.6(7)
C(38)-C(39)-C(40)	119.4(8)
C(41)-C(40)-C(39)	118.1(7)
C(40)-C(41)-C(42)	122.3(8)
C(41)-C(42)-C(37)	119.1(7)
C(47A)-C(48A)-C(43A)	120.0